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CONTENTS

Ions in Solution:

Some Aspects of the Present Status of the Thermodynamics of Electrolytic Solutions ..... HERBERT S. HARNED 623

The Conductance of Aqueous Solutions of Electrolytes .... DUNCAN A. MAC INNES 661

Solutions of Electrolytes in Non-Aqueous Solvents ..... CHARLES A. KRAUS 687

Kinetics in Ionic Systems ..... VICTOR K. LA MER 709

The Computation of Ionization Constants and Limiting Conductance Values from Conductivity Measurements ..... THEODORE SHEDLOVSKY 739

Notes from the National Bureau of Standards 745

The Franklin Institute Notes 751

Book Reviews 766

Publications Received 774

Current Topics 660, 708, 738, 744, 776

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IONS IN SOLUTION.*

SOME ASPECTS OF THE PRESENT STATUS OF THE THERMODYNAMICS OF ELECTROLYTIC SOLUTIONS.

BY

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INTRODUCTION.

Fifty years have passed since van't Hoff (86) made the monumental discovery that solutions which readily conduct the electric current possess freezing points, boiling points, osmotic pressures and vapor pressures which are characteristic of a special class of systems. van't Hoff realized that the investigation of these properties was a branch of the science of thermodynamics and made the first specialized application of thermodynamics to the subject. van't Hoff's treatment lacked generality and an exactness which might have been achieved if the system of thermodynamics developed by Gibbs (13) ten years earlier had been more generally known. From Gibbs, the theoretical physicist, and from van't Hoff, the chemist, came the realization that a science of solutions was only possible through development of the thermodynamics of solutions.

* Four addresses delivered at a symposium held Wednesday afternoon, March 16, 1938.

(Note—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

During the three following decades, numerous attempts to develop a system of solution thermodynamics which would be exact and sufficiently simple to reduce numerical computations to a minimum were made. Of these, the one which has been adopted almost universally was devised by Lewis (58). Indeed, the work of Lewis and his collaborators during the period from 1913–1928 may be said to have crystallized and integrated the theoretical and experimental parts of this subject into an exact science.

Simultaneously with this more and more detailed study of the thermodynamics of electrolytic solutions has evolved an electrostatic and hydrodynamical theory developed by statistical methods which is based on the great discovery of Arrhenius (7), also made fifty years ago, that ions exist in these solutions. The attempt to explain all the properties of these solutions by means of an ionic mechanism and the accompanying electrostatic fields serves further to emphasize the importance of obtaining an exact and comprehensive body of thermodynamic evidence which may be used for suggesting and testing any speculations regarding this state of matter.

The position of thermodynamics in relation to the general field of electrolytic solutions may be seen from a few general considerations. The first extremely important achievement of solution thermodynamics was to show that all the mechanisms used to determine equilibria in solutions may be employed to determine the same quantity. To be more explicit, measurements of the lowering of the freezing point, rise in boiling point, lowering of vapor pressure, osmotic pressure, solubility, or the electromotive forces of suitable cells may all be used to determine the Gibbs' chemical potential of an electrolyte, now usually denoted the relative partial molal free energy of the electrolyte, or what ultimately amounts to the same thing the relative partial molal free energy of the solvent. In other words, there are many experimental devices available for measuring the same fundamental quantity. This is extremely valuable for it is almost always possible to check and thus confirm the results obtained by entirely different mechanisms. Further, since relative partial heat contents, and heat capacities may be obtained from successive differentiation of the relative partial molal free energy, various comparisons of

electromotive force, vapor pressure data and so on may be made with heat of dilution and specific heat data. We shall show some of these comparisons determined by the various highly developed techniques of recent years, which will serve to illustrate the power of the method and the validity of the evidence so far obtained.

The very important relation between the relative partial molal free energy, $\bar{F} - \bar{F}_0$, and the interionic attraction theory of electrolytes may be shown by simple equations. Let

$$\bar{F} - \bar{F}_0 = RT \ln a, \tag{1}$$

where $\bar{F} - \bar{F}_0$ equals the partial molal free energy of an electrolyte relative to a suitable standard state, $\bar{F}_0$, and "a" its activity. "a" has the dimensions of a concentration and may be separated into two parts, the mean molality, $m_\pm$, and the activity coefficient, γ. Thus,

$$\bar{F} - \bar{F}_0 = \nu RT \ln m_\pm + \nu RT \ln \gamma, \tag{2}$$

where ν is the number of ions produced by dissociation of one molecule of electrolyte. In dilute solution, the term $\nu RT \ln m_\pm$ is the contribution to the partial free energy caused by the ions as uncharged ideal solutes. The term, $\nu RT \ln \gamma$, represents the contribution of all the effects of the Coulomb fields between all the ions, and any other interactions due to all the fields between ions and solvent molecules.

The modern theory of completely ionized electrolytes requires the fundamental relation between the rational activity coefficient, f_j, of an ion, its activity divided by the mole fraction, and the electric potential of the ion and its atmosphere, ψ_j. If e is the charge on the ion, then

$$\left.\frac{\partial A_{el}}{\partial N_j}\right]_{V,\,T} = \mu_j = \int_0^e \psi_j \, de, \tag{3}$$

where A_{el} is the electrical work in charging a gram molecule of ions, N_j, their number, and μ_j is the electrostatic contribution to the chemical potential of the single ion (17) (64). Since, $\mu_j = kT \log f_j$,

$$\log f_j = \frac{1}{kT}\int_0^e \psi_j \, de = \log \gamma_j + \log\left(1 + \frac{\nu M}{1000}\right), \tag{4}$$

where M is the molecular weight of solvent and k is Boltzmann's constant. For the condition that the potential is proportional to the charge,

$$\log f_j = \frac{e\psi_j}{2kT}. \tag{5}$$

The ion potential is the most fundamental of properties and the one probably most susceptible to theoretical interpretation. Consequently, its relation to f or γ shows how closely the development of the theory of electrolytes is associated with the experimental evaluation of such quantities.

The early period of experimental investigation, 1890 to 1915, may be said to have yielded very few results which are accurate enough for modern requirements. From 1915–1923, important advances were made in the development of experimental technique as for example the method of Adams (1) for freezing point measurement, the use of the Rayleigh manometer by Lovelace, Frazer and Sease (59) for measuring vapor pressure lowering, and the numerous improvements in cell technique. The first attempt by Lewis and Randall to bring together all available data was handicapped by not having available a universal and exact function which could be used for the necessary extrapolations to infinite dilution. This was supplied by the now famous theory of Debye and Hückel (12) in 1923, and from this time to the present, the accuracy of extrapolation has greatly increased. An important extension of this theory which aids in the treatment of solutions of polyvalent electrolytes, and of solutions of lower dielectric constant than water was made by Gronwall, LaMer, and Sandved (15). The last decade has witnessed great improvement and extension of the experimental investigations. Of these, we cite the extraordinary measurements of heats of dilution of Lange and his collaborators in Germany (56), and A. L. Robinson (72) in this country, the determinations of the partial molal heat capacities of electrolytes by Randall and Rossini (67) and Gucker Jr. (16), the extensive freezing point measurements of Scatchard and Prentiss (79), the development of the isopiestic differential vapor pressure method by R. A. Robinson (76) in New Zealand, and the very accurate

measurements of cells with liquid junctions carried out by Brown and MacInnes (10), and Shedlovsky and MacInnes (81).

The activity coefficient of an electrolyte is a function of many variables of which the concentration, the temperature, the dielectric constant and the pressure are the most important. Until recently, very few measurements of γ at temperatures other than 0° and 25° were available. Since 1932, systematic investigations have been made at Yale from which the activity coefficients of many univalent electrolytes, cadmium chloride (34) and sulphuric acid (37) in water have been measured at 5° intervals from 0° to 40° or 60° by electromotive force methods. During this time, Dr. Rodney P. Smith has perfected a boiling point apparatus by which the rise in boiling point may be measured with an accuracy of $\pm$ 0.0003°. By reducing the pressure, results may be obtained at temperatures between 60° and 100°. Thus, we have available methods which make possible investigations of the thermodynamics of these solutions from 0° to 100°.

To illustrate the effect of the change of dielectric constant upon the properties of an electrolyte, we have recently measured the electromotive force of the cells,

$$H_2 \,|\, HCl\ (m),\ \text{Dioxane}\ (X) - H_2O\ (Y) \,|\, AgCl - Ag$$

from 0° to 50° at 5° intervals, in 20 per cent. 45 per cent., 70 per cent. and 82 per cent. dioxane mixtures of dielectric constants of approximately 60, 40, 20, and 10. The molal acid concentration, m, was varied from 0.001 M to 3 M except in the cases of low dielectric constant when the acid at high concentration causes the separation into two layers. The dielectric constants of dioxane-water mixtures have been measured (4) and also the densities of all solutions. Simultaneously the conductances are being measured as well as the cells with liquid junctions from which we hope to obtain values for the transference numbers at equal activities of the acid. Over and above this fundamental study of the characteristics of a single electrolyte as a function of its concentration, the temperature and the dielectric constant, these measurements will make possible the accurate determination of the ionization constants of weak acids, bases and ampholytes in these media.

Good determinations of these quantities in non-aqueous media are practically non-existent.

The work described above has to do principally with those electrolytes which are highly dissociated in water. The use of cells without liquid junction with hydrogen and silver halide electrodes for the determination of the ionization constants of weak acids, bases and ampholytes, and the ionization of these substances in salt solutions has been developed at Yale and extended to the investigation of many electrolytes over wide temperature ranges. Further, very extensive investigations of the ionization of water in many salt solutions from 0° to 60° have been made.

In the following, a few examples of these results will be discussed in relation to the work of other laboratories. This will serve to give an impression of present state of the experimental aspects of the subject and the directions in which we may expect advances.

PART I.

COMPARISON OF THERMODYNAMIC PROPERTIES OF ELECTROLYTES DETERMINED BY VARIOUS METHODS.

Activity Coefficients of Potassium Chloride and Hydrochloric Acid in Water as Determined by Different Experimental Methods.

We shall begin by showing a few results which indicate the accuracy obtained with these kinds of measurements in recent years. The details of the methods of extrapolation have been given in the contributions to which references have been made, and will not be considered here. It will be sufficient if we state that all extrapolations were made by use of the Debye and Hückel equations.

Table I contains activity coefficients of potassium chloride at 0° and 25° determined from freezing point measurements and electromotive force data. The second column and third column contains values obtained from flowing amalgam cells at 0° by Harned and Cook (25), and Smith (82), respectively. The agreement is good from 0.1 to 3.5 M since the maximum error is about 0.1 mv. The results in the fourth column were computed by Spencer (84) from the best available data for freezing point lowering. The agreement indicates no error in freezing determinations greater than 0.0003° C. The first series of results at 25° were obtained by Harned and Cook from

TABLE I.
Activity Coefficients of Potassium Chloride.

m	0° [a]	0° [b]	0° [c]	25° [a]	25° [d]
0.005	(0.929)		(0.929)	(0.927)	(0.9275)
.01	(.904)		.903	(.901)	.902
.05	.819		.818	.815	.817
.1	.768	(.770)	.771	.769	.770
.2	.717	.717	.719	.719	.719
.3	.683			.688	
.5	.642	.642	.645	.651	.652
.7	.613	.615		.628	
1.	.588	.589	.590	.606	.607
1.5	.563	.562	.561	.585	
2.	.547	.548		.576	.578
2.5	.540	.541		.572	
3.	.539	.540		.571	.574
3.5	.540	.542		.574	.576
4.				.579	.581

[a] Harned and Cook, (25) E. M. F.
[b] Smith (82), E. M. F.
[c] Spencer (84), F. P.
[d] Shedlovsky and MacInnes (81), E. M. F. Cells with transference.

flowing amalgam cells, and the second by Shedlovsky and MacInnes (81) from cells with silver chloride electrodes and liquid junctions. The agreement throughout the entire range of concentration is excellent. These methods are quite different mechanically, and the method of Shedlovsky and MacInnes requires both the electromotive forces and independently determined transference numbers.

Another very close agreement between electromotive force and freezing point data occurs in the case of dilute hydrochloric acid solutions, and is shown in Table II. The second

TABLE II.
Activity Coefficients of Hydrochloric Acid at 0° from Electromotive Force and Freezing Point Measurements.

m	(E.M.F.)	(F.P.)
0.001	0.9668	0.9661
.002	.9541	.9534
.005	.9304	.9300
.01	.9065	.9064
.02	.8774	.8772
.05	.8346	.8341
.1	.8027	.8021
.2	.7756	.7754
.5	.775	.774
1.	.842	.840

column contains the values obtained by Harned and Ehlers (30) from cell measurements and the third results computed by Randall and Young (69) from Randall and Vanselow's (68) freezing point measurements. Both extrapolations were made with the Debye and Hückel limiting equation, and the values of γ were evaluated at round concentrations from smooth curves drawn through the experimental results. The agreement between the values obtained by the two methods is remarkably good.

The Thermodynamics of Aqueous Sodium Chloride Solutions in Water.

Solutions of sodium chloride in water have been investigated by all available methods so that a good estimate of its properties may be obtained from 0° to 100°. Because of the very accurate measurements of Brown and MacInnes (10) of cells with liquid junctions, we have an exact reference value at 25°. Further Gulbranson and A. L. Robinson (72) have determined the relative partial molal heat content, $\bar{L}_2$, from 10° to 25° with a high order or accuracy and at sufficient dilution for accurate extrapolation. Their values of $\bar{L}_2$ at 0.1 M are given as a function of temperature by the equation,

$$\bar{L}_{2(0.1)} = -1277 + 4.62\,T. \qquad (6)$$

Now, γ is related to $\bar{L}_2$ by the exact equation,

$$2\frac{\partial \ln \gamma}{\partial T} = -\frac{\bar{L}_2}{RT^2}. \qquad (7)$$

Upon substitution of $\bar{L}_2$ given by equation (6) in equation (7), integration and evaluation of the integration constant by employing Brown and MacInnes' value of 0.7784 for γ at 0.1 M and 25°, we find

$$-\log \gamma_{0.1} = \frac{139.56}{T} + 1.1625 \log T - 3.2358. \qquad (8)$$

Values of $\gamma_{0.1}$ at various temperatures computed by this equation are given in the second column of Table III.

An entirely independent check of these results may be obtained from the electromotive forces of cells without liquid junction of Harned and Nims (49) by employing the extended

TABLE III.

The Activity Coefficient of Sodium Chloride at 0.1 M by Independent Methods.

t.	$\gamma_{0.1}$ (Eq. 8).	$\gamma_{0.1}$ (Eq. 9).	$\gamma_{0.1}$ (B.P.).
0	0.7809	0.781	—
10	.7807	.782	—
20	.7793	.781	—
25	(.7784)	.779	—
30	.7773	.776	—
40	.7743	.773	—
50	.770	—	—
60	.766	—	0.766
70	.761	—	.762
80	.756	—	.757
90	.751	—	.752
100	.745	—	.746

Debye and Hückel equation,

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + Bc - \log (1 + 0.036\, m) \qquad (9)$$

over the concentration range 0.1 to 1 M. μ is the universal isothermal constant of the theory, A the parameter which accounts for the finite size of ions and B is a constant. Values at $\gamma_{0.1}$ computed by this means are given in the third column of the table. The agreement is within $\pm$ 0.001 at nearly all the temperatures.

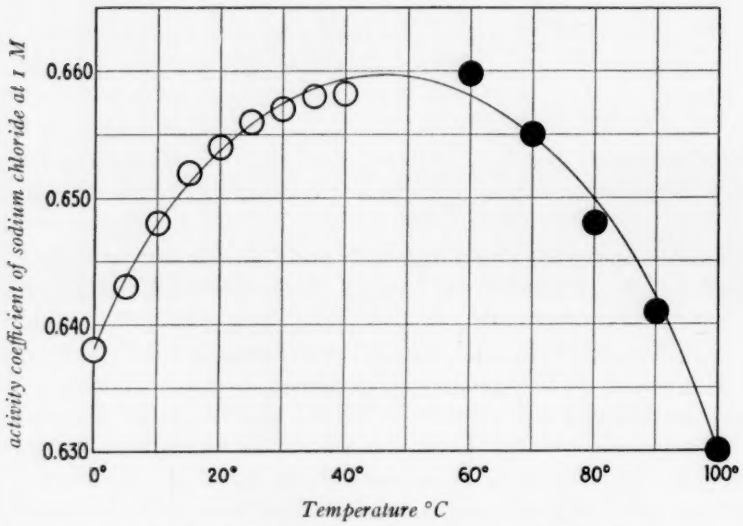
Very recently, Dr. R. P. Smith in this laboratory has succeeded in measuring the rise of boiling point of salt solutions with an accuracy of the order of $\pm$ 0.0003°. These measurements allow good determinations of γ at 100° and at concentrations from 0.1 M to the saturated solutions. Further by reducing the pressure Dr. Smith has obtained results of the same accuracy at 90°, 80°, 70°, and 60°. Due to his kindness, the results from his preliminary extrapolations are included in the fourth column of the table. The agreement with those computed by equation (8) is very good indeed.

A further confirmation of the agreement of the boiling point results with those obtained by electromotive force measurements is apparent from inspection of Fig. 1. Here γ of sodium chloride at 1 M concentration is plotted against temperature. The values from 0° to 40° were obtained from the electromotive forces of cells without liquid junction con-

taining flowing sodium amalgam and silver chloride electrodes, and the values from 60° to 100° were obtained from boiling point measurements.

There seems to be a slight discrepancy in the two series between 40° and 60° which indicates that possibly the result from electromotive force at 40° is too low, and that from boiling point measurements at 60° is too high. But when it is pointed out that the diameter of the dots is 0.002 in γ, it

FIG. 1.



The Activity Coefficient of 1 M Sodium Chloride from 0° to 100°.

○ Electromotive Force
● Boiling Point Rise

appears that the maximum discrepancy is of the order of 0.1 mv. and less than 0.001° in boiling point rise.

Comparison of the Activity Coefficients of Sodium and Potassium Chlorides as Determined by Electromotive Force and Isopiestic Vapor Pressure Measurements.

A very valuable contribution to the thermodynamics of electrolytes in aqueous solution at 25° has been made recently by Robinson and Sinclair (76), and Robinson (72) (73) (74) (75) who perfected the isopiestic vapor pressure method for the determination of the osmotic and activity coefficients.

This is a differential method whereby vapor equilibrium is attained at constant temperature between two solutions, one of which is employed as a standard of reference. Thus, if the activity coefficient of one electrolyte which is nonvolatile is known, that of another electrolyte may be readily obtained. Their apparatus consisted of four square silver dishes which were brought into thermal contact along their sides and which rested on a heavy copper block. To attain the closest possible contact, the sides were carefully ground together and polished, and then all the dishes were ground and polished on the block. The apparatus was then placed in a dessicator and rocked in a thermostat. At the beginning of an experiment two of the dishes contained a weighed sample of the standard solution of known strength and the other two dishes a weighed sample of a known concentration of the solution of the electrolyte to be investigated. After equilibrium occurred through the vapor phase which usually took forty-eight hours, the dishes were weighed. This is all that is necessary to obtain the concentration ratios of two isopiestic solutions. Knowing the activity coefficient of the reference solutions, it is a simple matter to determine that of the other from a number of these ratios at different concentration ranges.

Robinson has determined the activity coefficients of many electrolytes at 25° among which were a number not susceptible readily to investigation by other methods. The accuracy of this method of differential vapor pressure measurement is very high, and the results at 25° agree very closely with those determined by electromotive force methods. A further advantage of the vapor pressure method is its universality when measuring salts in a given solvent.

We shall cite one comparison between activity coefficients derived from electromotive force, and those derived from the isopiestic vapor pressure measurements. Dr. Robinson has very kindly permitted the inclusion of his computations of the activity coefficients of sodium and potassium chloride at 15°, 20° and 25° in Table IV. The activity coefficients of sodium chloride at 15° and 20° were computed by using as reference the activity coefficients of potassium chloride from the electromotive forces of Harned and Cook (25). The second and fourth column contain the values of the activity coefficients of

TABLE IV.

The Activity Coefficients of Potassium and Sodium Chlorides by Cell Measurement and Isopiestic Vapor Pressure Method.

m	NaCl				KCl			
	15[a]	15[b]	20[a]	20[b]	25[a]	25[b]	25[c]	25[d]
0.1	0.777	0.778	0.779	0.778	0.770	0.770	0.770	—
.2	.732	.732	.733	.732	.719	.720	.719	—
.3	.705	—	.708	—	.688	.689	—	—
.5	.676	.677	.780	.679	.651	.652	.652	—
.7	.659	—	.665	—	.628	.629	—	—
1.	.649	.650	.655	.654	.607	.607	.607	.605
1.5	.647	.646	.653	.651	.586	.586	—	(.586)
2.	.656	.657	.664	.664	.577	.577	.578	.577
2.5	.674	.675	.683	.683	.574	.573	—	.574
3.	.700	.701	.709	.711	.576	.572	.574	.575
3.5	.732	.733	.740	.743	.579	.576	.576	.578
4.	.768	.770	.776	(.782)	.586	.586	.581	.583
4.5	—	—	—	—	.591	—	—	.590
4.8	—	—	—	—	.598	—	—	.599

[a] Isopiestic vapor pressure.
[b] Flowing amalgam cells.
[c] Cells with liquid junction.
[d] Rayleigh manometer.

sodium chloride obtained from this reference by the isopiestic vapor pressure method. The third and fifth column contain the same quantity computed from the electromotive force data of Harned and Nims (49). From 0.1 M to 3.5 M, the agreement between the two sets of values is remarkably good. The last four columns contain activity coefficients of potassium chloride computed by the different methods from the activity coefficients of sodium chloride as reference. These reference values were evaluated from the data of Harned and Nims. The results in the sixth column were obtained from isopiestic vapor pressure measurement, in the seventh from flowing amalgam-silver chloride cells, the eighth from cells with transference measured by Shedlovsky and MacInnes (81), and the last column values from the direct vapor pressure measurements of Lovelace, Frazer and Sease (59). The agreement throughout is excellent. The development and use of the isopiestic vapor pressure measurements in the hands of Dr. Robinson has been of very great value in this field. Indeed,

many more important results may be expected in the near future.

The Relative Partial Molal Heat Content from Heat of Dilution and Electromotive Force Data.

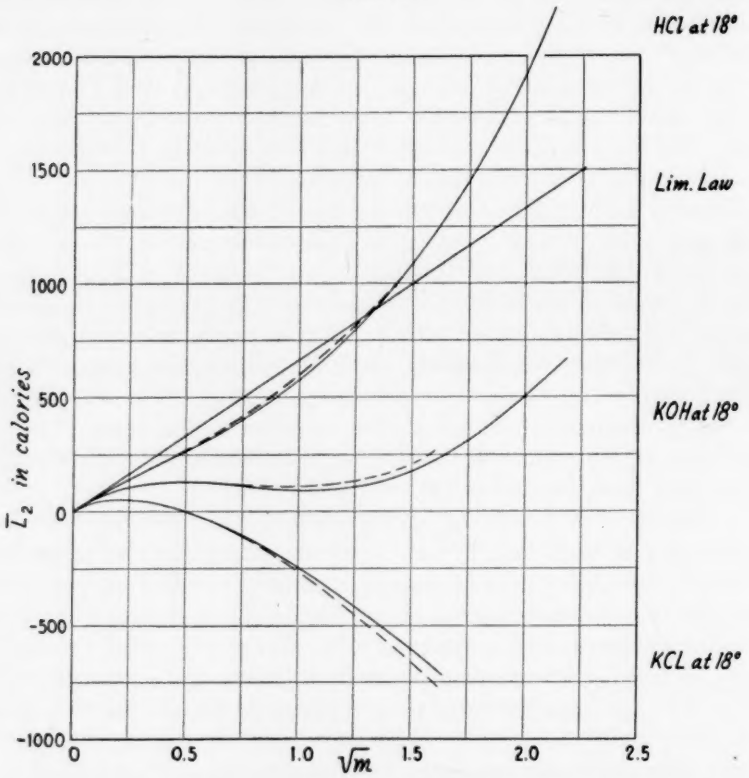
Due principally to the extraordinarily accurate determinations of the integral heats of dilution of the solutions of many electrolytes which have been carried out by Lange and his collaborators (56), there are now available accurate results of the relative partial molal heat contents of these substances in aqueous solution at 18° and 25°. This quantity may be calculated also from electromotive force measurements by means of the Gibbs-Helmholtz equation and the limiting equations of the Debye and Hückel theory provided these latter have been obtained with sufficient accuracy over a wide enough range of temperature. Since an error of 1 microvolt per degree in temperature coefficient of electromotive force of cells without liquid junction containing a uniunivalent electrolyte causes an error of 7 cals. in $\bar{L}_2$, the relative partial molal heat content of the electrolyte, we cannot contend that this is the best method for the evaluation of this quantity. On the other hand, if electromotive forces yield results which agree closely with those determined calorimetrically, we have further evidence of their fundamental validity.

Figure 2 contains plots of the values of $\bar{L}_2$ obtained by the two methods at the higher concentrations for the cases of potassium chloride, potassium hydroxide and hydrochloric acid solutions in water at 18°. The solid lines represent the values determined by electromotive forces (25) (24) (30) and the dashed curves those obtained from heat of dilution data (77). The maximum discrepancy between the two sets of data is about 60 cals. This agreement is quite good since the flowing alkali amalgam cells employed in two cases are among the most difficult cells to operate. The straight line represents the limiting law of the Debye and Hückel theory. Similar results have been obtained for sodium chloride (49), bromide (27), sodium hydroxide (39), hydrobromic acid (44), zinc sulphate solutions (11) (22), and sodium sulphate solutions (40).

A more spectacular case is that of sulphuric acid, an electrolyte which is partially ionized and for this reason approaches

the limiting slope of the Debye and Hückel theory only in extremely dilute solutions ($m < 0.0001$). In Fig. 3 are given the values of $\bar{L}_2$ determined by Lange, Monheim and Robinson (57) calorimetrically, and those determined from electromotive force measurements in dilute and concentrated solutions by

FIG. 2.



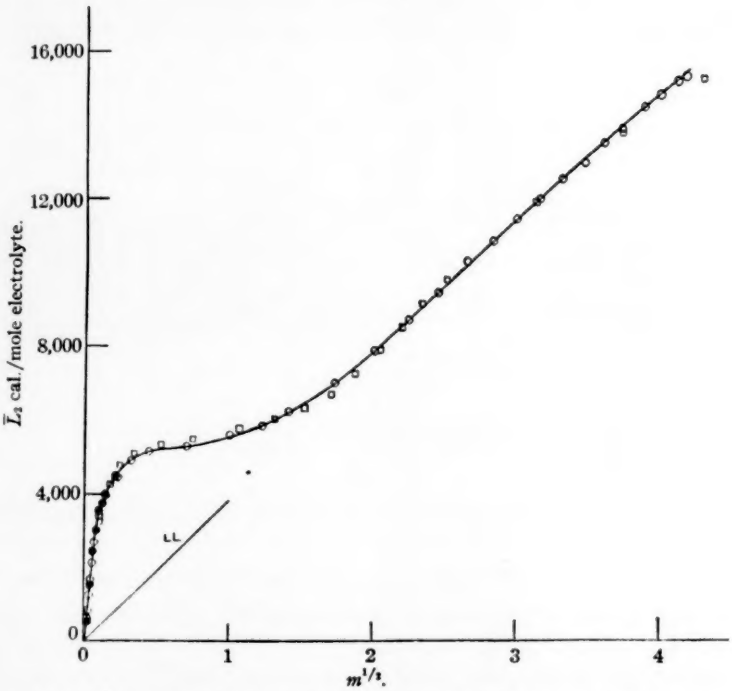
The Relative Partial Molal Heat Contents of Potassium Chloride, Potassium Hydroxide and Hydrochloric Acid at 25°.

Harned and Hamer (37), and in concentrated solutions by Brönsted (9). The cells employed by Harned and Hamer were of the types:

$$H_2 | H_2SO_4\ (m) | PbSO_4 - PbO_2 - Pt,$$
$$H_2 | H_2SO_4\ (m) | Hg_2SO_4 - Hg,$$

whereas Brönsted employed the latter. The first of these cells gives reliable results in the more dilute solutions (0.0005 *M* to 0.05 *M*). At higher concentrations, both cells are reliable. They differ in cell reaction since the first involves the production of two mols of water.

FIG. 3.

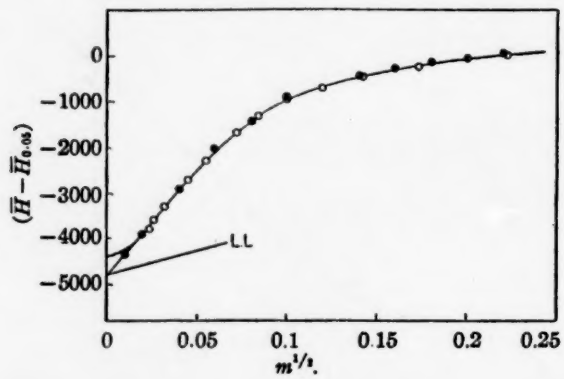


$\bar{L}_2$ *vs.* $m^{\frac{1}{2}}$ from 0 to 17.5 M at 25°: ○, e.m.f.; ●, calorimetric; □, e.m.f. (Brönsted)

The rapid increase of $\bar{L}_2$ in the very dilute solutions is characteristic of the behavior of an incompletely ionized electrolyte. In this case, it is very much greater than that predicted by the limiting law. The agreement between the values determined by the electrometric and calorimetric methods is shown more clearly in Fig. 4 where the results in dilute solution (0.0001 *M* to 0.05 *M*) are shown. The dots represent the calorimetric values, and the circles the values

from the electromotive forces. The agreement is excellent since the deviation between the two series of results is within ± 30 cals. There is a difference, however, in the method of extrapolation employed. Lange, Monheim and Robinson used an empirical straight line extrapolation while Harned and Hamer fitted their results to the limiting theoretical requirement of the Debye and Hückel theory. This causes a discrepancy of 460 cals. A more exact extrapolation will be very difficult since accurate results below 0.0001 M will be required.

FIG. 4.

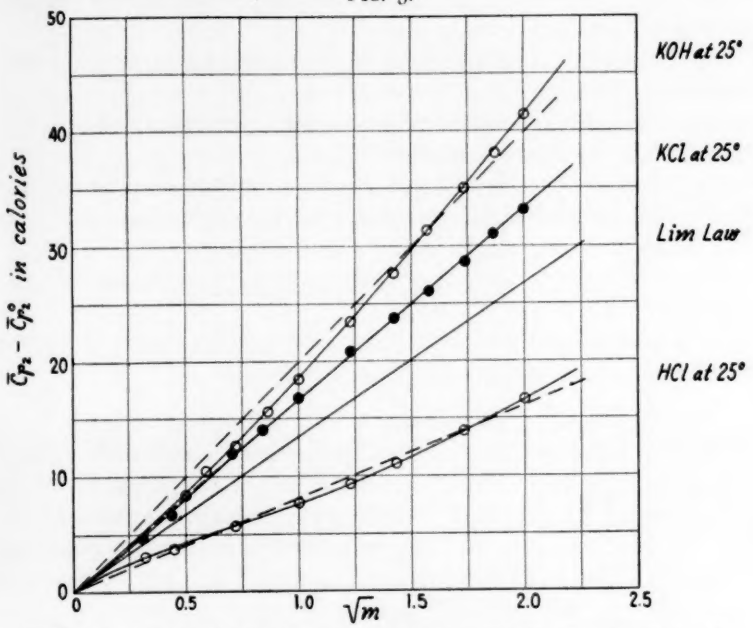


$(\bar{H}_{0.05} - \bar{H})_{25}$ *vs.* $m^{\frac{1}{2}}$ in dilute solutions: ○, e.m.f.; ●, Lange, Monheim and Robinson, calorimetric

The Relative Partial Molal Heat Capacity from Calorimetric and Electromotive Force Data.

The partial molal heat capacity of electrolytes has also received considerable attention in recent investigations. Randall and Rossini (67) have determined this quantity for a number of electrolytes and more recently Gucker and Schminke (16) have evaluated it. Fig. 5 contains plots of the relative partial molal heat capacity ($\bar{C}_p - \bar{C}_{p_0}$) of potassium chloride, potassium hydroxide and hydrochloric acid as determined by the calorimetric measurements (78) and from electromotive force data (25) (24) (30). The dashed lines represent the calorimetric values whereas the dots, circles and crosses are the values determined from suitable cells. The agreement is excellent since the maximum deviation is of the order of two calories.

FIG. 5.



The Relative Partial Molal Heat Capacities of Potassium Chloride, Potassium Hydroxide and Hydrochloric Acid in Water

PART II.

IONIC EQUILIBRIA WHICH INVOLVE WEAK ELECTROLYTES IN SALT SOLUTIONS.

The Ionization of Water From the Electromotive Force of Cells Without Liquid Junction.

In a series of investigations (19) (42) (54) it was shown that the ionic activity coefficient and ionization of water could be determined in neutral salt solutions from cells without liquid junctions. More recently (71) (35) (52) (26) (36) (46) (28) (38) (45), these measurements have been extended for many salts over wide concentration and temperature ranges by employing cells of the types,

$$H_2 | MOH\ (M_1),\ MX\ (m) | AgX - Ag, \qquad (A)$$

$$H_2 | HX\ (m_1),\ MX\ (m) | AgX - Ag, \qquad (B)$$

where X represents Cl, Br, and I, and M represents Na, K, and Li. It has been shown that much valuable information may be obtained from these data as for example:

(1) The ionization constant of water.

(2) The normal potential of the silver-silver halide electrode.

(3) The activity coefficient of the halide acids in the halide solution.

(4) The ionic activity coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, in the salt solutions.

(5) The ionization of water, $m_H m_{OH}$, in the halide solutions.

(6) The relative partial molal heat content, specific heat and entropy of the acids in the salt solutions.

(7) The heat of ionization, entropy and specific heat of the reaction: $H_2O = H^+ + OH^-$.

(8) The heat of ionization of water, and the relative partial molal heat of ionization in the salt solutions.

The details of this method of investigation of such ionic equilibria have been described elsewhere, and only a few examples which illustrate the character of the results will be mentioned. In the first place, these measurements yield a very accurate means for determining the ionization constant of water. The equation for a cell of Type (A) may be written,

$$E_A = E_0 - \frac{RT}{NF}\ln \gamma_H\gamma_X\, m_H m_X, \qquad (10)$$

where E_A is the electromotive force, E_0 the standard electromotive force of the cell, R the gas constant, T the absolute temperature, F the Faraday, N the Faraday equivalents, and γ_H, γ_X, m_H, m_x are the activity coefficients and concentrations of the species denoted by subscripts. The hydrogen ion concentration, m_H, may be eliminated from this equation by the thermodynamic equation for the ionization of water, namely,

$$K = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} m_H m_{OH}, \qquad (11)$$

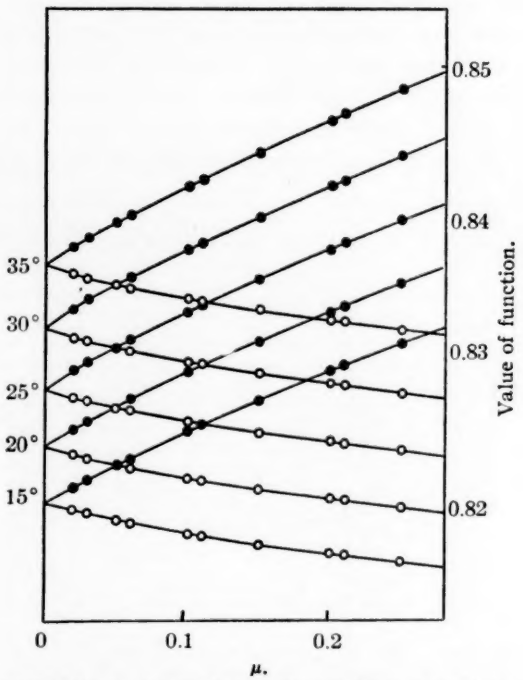
to give the equation

$$E_A - E_o + \frac{RT}{NF}\ln \frac{m_X'}{m_{OH}'} = \frac{RT}{NF}\ln \frac{\gamma_H\gamma_{OH}}{\gamma_H\gamma_{Cl}a_{H_2O}} - RT\ln K. \qquad (12)$$

If the standard potential of the cell, E_o, is known from measurements of the cells of type (B) either with or without salt,

K can readily be evaluated by this equation by extrapolation to infinite dilution. The left side is known since E_0 and the m_{Cl} and m_{OH} are known. Further, since all activity coefficients and the activity of water are unity at infinite dilution, the first term on the right vanishes at m equals zero. Therefore, if the left side be plotted versus m, then its value at zero m equals $-RT \ln K$. If the equations of the two cells be combined with the limiting law of the theory of Debye and

FIG. 6.



Illustrating the extrapolation of the dissociation constant of water by equation (12) and also by equation (13): ○, equation (12); ●, equation (13).

Hückel with an added linear term, the ionization constant may be determined without a previous knowledge of E_0. The resulting equation takes the form

$$E_A - E_B - \frac{RT}{NF} \ln \frac{m_H'' m_X'' m_{OH}'}{m_X'} + \frac{RT}{NF} \frac{5.908 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} = -\frac{RT}{NF} \ln K + \beta\mu, \quad (13)$$

where m_H'', m_X'' are the concentrations of the hydrogen and chloride ions in cell (B), m_{OH}', m_X', the hydroxide and halide ion concentrations in cell (A), μ is the ionic strength, β an empirical constant and D is the dielectric constant of water. The left side is known from the measurements, and it is clear that its value at μ equals zero is $-\frac{RT}{NF}\ln K$.

Both of these extrapolations are illustrated by Fig. 6 taken from measurements of the cells containing hydrochloric acid and lithium chloride (26). The circles represent extrapolations according to equation (12) and the dots by the method according to equation (13). These curves have slopes of opposite sign and converge nicely to the same limiting value.

Values of K determined at different times with different cells from 0° to 50° are compiled in Table V. The sixth

TABLE V.

The Ionization Constant of Water.

$K \times 10^{14}$.

t / Salt.	KCl.	NaCl.	LiBr.	$BaCl_2$.	Mean.	Mv.
0	(0.115)	0.1134	0.1132	(0.1125)	0.1133	0.50
5	(.185)	.1850	.1842	(.1834)	.1846	.33
10	(.293)	.2919	.1921	(.2800)	.2920	.33
15	(.452)	.4505	.4504	.4500	.4503	.11
20	.681	.6806	.6806	.6815	.6809	.03
25	1.008	1.007	1.007	1.009	1.008	.05
30	1.471	1.470	1.467	1.466	1.468	.09
35	2.088	2.091	2.088	2.090	2.089	.03
40	2.916	2.914	(2.891)	2.920	2.917	.26
45	4.016	4.017		4.023	4.018	.04
50	5.476	5.482		5.465	5.474	.07

column contains the mean value and last column the total deviation of all the values of K calculated to millivolts. The largest discrepancies occur at the three lower temperatures, and the results are such as to indicate that the values in parenthesis are in error. If these be discarded, the maximum error is ± 0.05 mv. or ± 0.1% in K.

The Ionic Activity Coefficient Product and Ionization of Water in Halide Solutions.

The activity coefficient of the halide acid in the salt solution may be obtained from the electromotive force of cell B by

means of the equation,

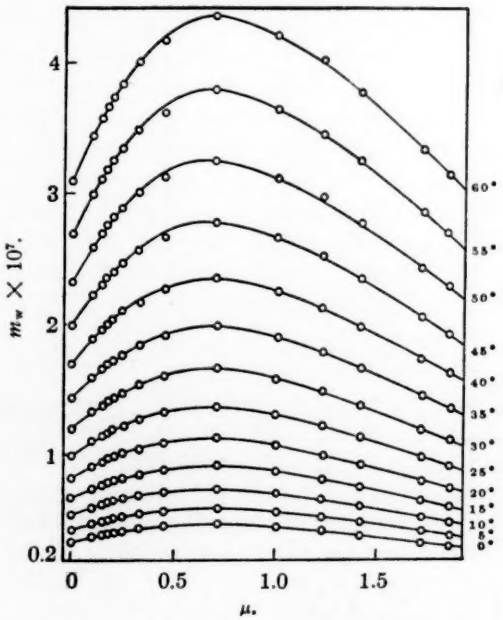
$$2 \log \gamma_{HX} = -\frac{F}{RT}(E_B - E_0) - \ln m_H'' m_X'' \qquad (14)$$

and the ionic activity coefficient product of water, $\frac{\gamma_H \gamma_{OH}}{a_{H_2O}}$, or $\frac{K_w}{m_H m_{OH}}$ by the equation obtained by combining this expression with equation (12), or

$$\log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \log \frac{K_w}{m_H m_{OH}} = \frac{F}{RT}(E_A - E_B) - \ln \frac{m_H'' m_X'' m_{OH}'}{m_X'} + \ln K_w. \qquad (15)$$

Since K_w has been evaluated by the method of the preceding section, $\gamma_H \gamma_{OH}/a_{H_2O}$, and $m_H m_{OH}$ in the salt solutions may be obtained from the measurements of E_A and E_B. We have

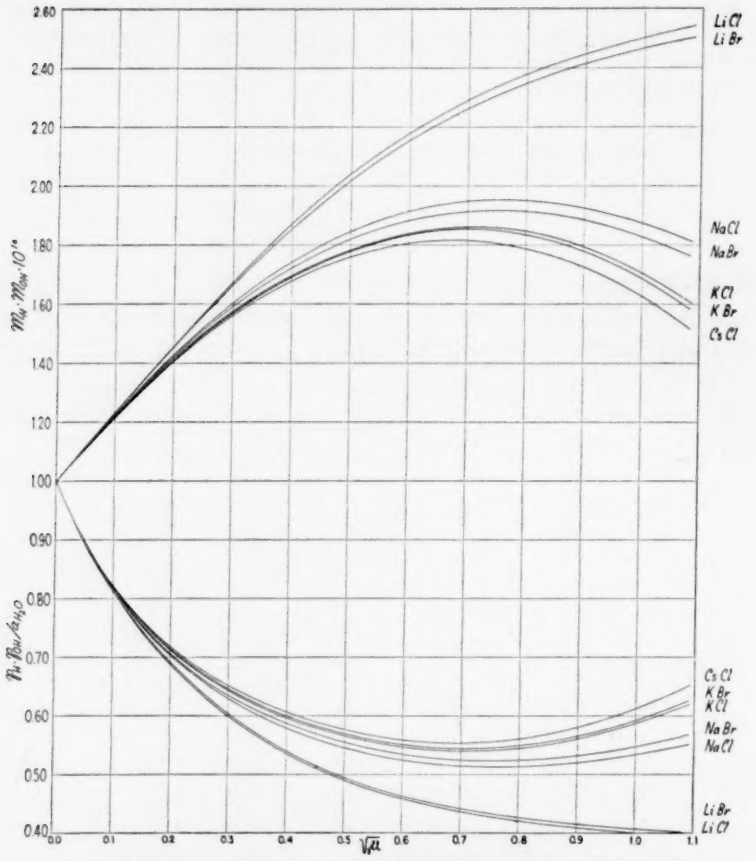
FIG. 7.



The dissociation of water in potassium chloride solutions.

carried out extensive investigations of these quantities in solutions of chlorides and bromides of potassium, sodium and lithium and barium chloride over a concentration range from 0 to 4 M and at temperatures from 0 to 50° or 60°.

FIG. 8.



The Ionic Activity Coefficient Product and Ionization of Water in Alkali Chloride and Bromide Solutions at 25°.

The effect of temperature and concentration on m_w or $\sqrt{m_H m_{OH}}$ is illustrated by Fig. 7 where plots of the values for potassium chloride solutions are given. The isothermals show a maximum at about 0.7 M.

In Fig. 8 values of both $\gamma_H \gamma_{OH}/a_{H_2O}$ and $m_H m_{OH} \times 10^{14}$

are plotted versus $\mu^{1/2}$ for a series of alkali halides at 25°. The arrangement of the graphs show one interesting characteristic. At concentrations where differences are perceptible it is found that the ionization is in the order of lithium chloride, bromide, sodium chloride, bromide, potassium chloride, bromide, and cesium chloride, being greatest for the first salt of this series. This is in the order of the quantity $\left(\frac{1}{a_+} + \frac{1}{a_-}\right)$ where a_+ and a_- are the ionic radii, determined from crystallographic data. This is the expected result, namely that the water molecule should be ionized most readily by the ions of smaller radii since they can approach these ions to closer distances and consequently be subjected to stronger fields.

The Total Heat of Ionization of Water in Potassium and Sodium Chloride Solutions.

If the value of $(E_A - E_B)$ in equation (15) be substituted in the Gibbs-Helmholtz equation, the expression

$$\Delta H = RT^2 \frac{d \ln K}{dT} - RT^2 \frac{d \ln \gamma_H \gamma_{OH} / a_{H_2O}}{dT} \qquad (16)$$

is obtained. The first term on the right is the heat of ionization ΔH_i at constant temperature and pressure in pure water, while the second term is the relative partial molal heat content of the species designated in the salt solutions.

Values of ΔH determined from the electromotive force measurements are plotted against $\mu^{1/2}$ in Fig. 9. The solid lines represent the results obtained from electromotive forces whereas the values represented by circles and dots are the values determined by Richards and Rowe (70) from calorimetric experiments of the heat of dilution. The agreement is good. The extrapolated value from calorimetric data is less than that obtained from the electromotive force measurements. This difference may be explained by consideration of the difference in units of concentration employed. The values of K from electromotive force data are in molalities. Since at zero salt concentration, the normal concentration equals the molality times the density of pure solvent, the ionization constant, K_c, is equal to Kd_0. Therefore

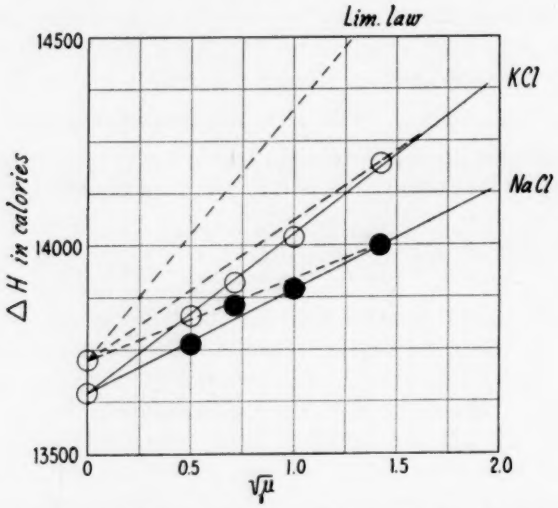
$$RT^2 \frac{d \ln K}{dT} = RT^2 \left[\frac{d \ln K_c}{dT} - \frac{1}{d_0} \frac{d d_0}{dT} \right]$$

or

$$\Delta H_i = \Delta H_{i(c)} - \frac{RT^2}{d_0}\frac{d\,d_0}{dT}. \qquad (17)$$

The second term on the right is of the order of 40–50 cals. at 20 to 25°, and therefore, $\Delta H_i = \Delta H_{i(c)} + 50$ cals., which is approximately the difference found between the calorimetric and the electromotive force results. This question will require

FIG. 9.



Total Heat of Ionization of Water in Sodium and Potassium Chloride Solutions at 20°.

further careful consideration before a final verdict can be given.

Ionization of Weak Acids, Hydroxides and Ampholytes from the Electromotive Forces of Cells without Liquid Junction.

In recent years, we have devoted considerable effort in developing and extending the method of determining the ionization constants of weak electrolytes and the ionization of weak acids in salt solutions from cell measurements which do not involve liquid junction potentials. Two types of cells have been employed in these investigations which may be classified as buffered and unbuffered. As an example of these

cells we cite the ones employed for studying weak acids, HAc, represented by

$$H_2|HAc\ (m_1),\ NaAc\ (m_2),\ NaCl\ (m_3)\,|AgCl - Ag$$

and

$$H_2|HAc\ (m_1),\ NaCl\ (m_2)\,|AgCl - Ag.$$

The first of these is the more convenient for the determination of the ionization constant since the results obtained by it may be extrapolated very readily. The equation for the electromotive force in a form suitable for purposes of extrapolation (31) is,

$$\frac{F}{2.3026\,RT}(E - E_0) + \log\frac{(m - m_H)m_3}{(m_2 + m_H)} = \log\frac{\gamma_H\gamma_{Cl}\gamma_{HAc}}{\gamma_H\gamma_{Ac}} - \log K \quad (18)$$

where K is the ionization constant of the acid, and γ and m are the activity coefficients and concentrations of the species denoted subscripts. E_0 is the standard potential obtained from the electromotive forces of the cells,

$$H_2|HCl\ (m)\,|AgCl - Ag$$

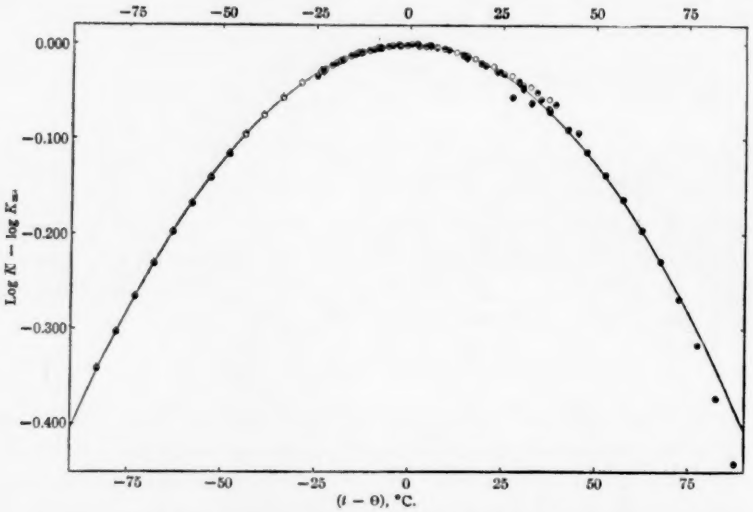
The left hand side of this equation may be readily evaluated if E_0 is known, and its value at zero ionic strength is $-\log K$ since the term containing the activity coefficients vanishes when μ equals 0. Plots of the left side versus μ are straight or nearly so, and vary little in magnitude with μ so that extrapolations are readily made (31) (32) (61).

The unbuffered cell containing the weak acid can be used to determine ionizations constants, but is not so suitable for that purpose as the buffered cell. On the other hand, when combined with data obtained from cells of the same type containing a strong acid, it can be used for determining the ionization constant and ionization of the weak acid in the salt solutions (51) (50) (41). The rather complex thermodynamics of this cell has been thoroughly discussed elsewhere (50) (41) and it will be sufficient to state that both $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ and $m_H^2/M - m_H$ in salt solutions may be obtained from the electromotive forces of this cell. A plot of these quantities in the case of acetic

acid against $\mu^{1/2}$ is quite similar that of $\gamma_H\gamma_{OH}/a_{H_2O}$ and $m_H m_{OH}$ shown in Figs. 7 and 8.

Recently, the ionizations of numerous weak acids, bases and ampholytes have been determined from the measurements of the buffered cells. These include such widely varying types of weak electrolytes as acetic (31), propionic (31), butyric (53), and chloroacetic acid (87), glycine (65), alanine (63) and other ampholytes, (62) HPO_4^{--} (61); $H_2PO_4^-$ (61);

FIG. 10.



The graph of $\log K - \log K_m$ against $(t - \theta)$: ◒ glycine (K_B), ◇ glycine (K_A), ◒ formic acid, □ alanine (K_A), ♀ $H_3PO_4^-$, ○ acetic acid, ◓ propionic acid, ♀ chloroacetic acid, ● HSO_4^-. The smooth curve represents equation (2) where $p = 5.0 \times 10^{-5}$. Diameter of circles representing points corresponds to 1% of the value of K.

HSO_4^- (18), metaboric acid (65) and others (62) (43). The measurements were carried out over temperature ranges (0° to 50°) which were as extensive as the experimental restriction permitted without loss of accuracy.

That the variation of the ionization constant with temperature can be expressed by a uniform function is strikingly shown by a graph due to Harned and Embree (33). (Fig. 10). Many of these ionization constants show a maximum at a given temperature. Here $\log K - \log K_m$ is plotted against $(t - \theta)$ where K_m is the maximum value of the ionization

constant and θ is the temperature at which the ionization is a maximum. All the results fit this curve very closely and in fact in the neighborhood of the maximum (within $\pm$ 75°) the curve is parabolic. Its equation is,

$$\log K - \log K_m = -5 \times 10^{-5}(t - \theta)^2. \qquad (19)$$

This result gives the ionization constant in terms of two empirical constants, K_m and θ and one universal constant, 5×10^{-5}. Its form is very simple for use in numerical computations.

From this relation, it follows that the heat of ionization is given by,

$$\Delta H = -4.575 \times 10^{-4} T^2(T - \theta) \qquad (20)$$

and the specific heat of the reaction, ΔC_p, by

$$\Delta C_p = -4.575 \times 10^{-4} T(T + 2(t - \theta)), \qquad (21)$$

This equation leads to negative values of ΔC_p which are of the order $-$ 40 cals. at 298°. Further the entropies of the reactions are of a magnitude of $-$ 20 cals.

Very recently, Pitzer (66) has shown that this value of entropy is in accord with theoretical considerations concerning the entropy change in reactions of the type $HA = H^+ + A^-$. By employing the customary thermodynamic equations involving the change in heat content, entropy and heat capacity, and by taking ΔC_p as $-$ 40 cals., Pitzer also obtains an equation with two arbitrary constants, A and B,

$$\log K = A + \frac{B}{T} - 20 \log T. \qquad (22)$$

He shows that in cases where K and T are in the neighborhood at 25° C., this equation gives essentially the same results as equation (21). In other cases, such as that of water which possesses a maximum of ionization at 300°, the latter equation is the closer approximation.

Before leaving this subject of weak electrolytes, it seems appropriate to draw attention to the recent strides towards exact data obtained by the improved conductance method (60) and the method outlined above. In the forty-three pages in International Critical Constants Tables devoted to ionization

constants of weak electrolytes there are very few results which can be relied on to within narrow limits. For example, the ionization constant of formic acid at 25° is given as 2.1×10^{-4} whereas the value of this quantity is $1.773 \pm 0.005 \times 10^{-4}$. Further, the values given at different temperatures are very inaccurate. Indeed, in a few cases where data are given, the results are so inaccurate that many of the points fall completely outside the paper on which as sensitive a graph as Fig. 10 is drawn. The results in the tables give order of magnitude only and cannot be used for modern theoretical requirements.

PART III.

SOME CONSIDERATIONS CONCERNING THE THERMODYNAMICS OF ELECTROLYTES IN NON-AQUEOUS SOLVENT-WATER MIXTURES.

The Evaluation of the Standard Potential of the Hydrogen-Silver Chloride Cell in Dioxane-Water Mixtures.

In the introduction, we have mentioned that a technique has been developed and extensive and accurate measurements of the cell,

$$H_2 | HCl\ (m),\ \text{Dioxane}\ (X),\ H_2O\ (Y) | AgCl - Ag,$$

have been made in media of dielectric constants from that of pure water ($D_{25} = 78.54$) to that of an 82% dioxane-water mixtures ($D_{25} = 9.57$). These experiments are being extended to lower acid concentrations and to media of lower dielectric constant, and have not been fully calculated (47) (48) (20) (23) (29).

The crux of the problem is one of extrapolation which becomes increasingly difficult as the dielectric constant decreases. In media of dielectric constant greater than 15, we have succeeded in obtaining values of the standard potential which appear to be quite accurate. In the still more concentrated dioxane mixtures, results at concentrations of acid in the range, 0.00005 to 0.001 M, will be necessary for this purpose and these are difficult to obtain experimentally. If E_0 is known, then the thermodynamics of the acid in such mixtures may be developed accurately. Further, this quantity and electromotive forces of cells of the type discussed in the preceding section will make possible the accurate determination of the ionization constants of weak electrolytes in non-aqueous solvents, a field which has hardly been investigated at all.

A convenient form of equation for purposes of extrapolation may be derived from the equation of cell and the equation of the theory of Debye and Hückel. It is,

$$E' = E + 2k \log m - \frac{2ku\sqrt{c}}{1 + A\sqrt{2c}} - 2 \log (1 + 0.002\, G_0 m) = E'_0 + f(m), \quad (23)$$

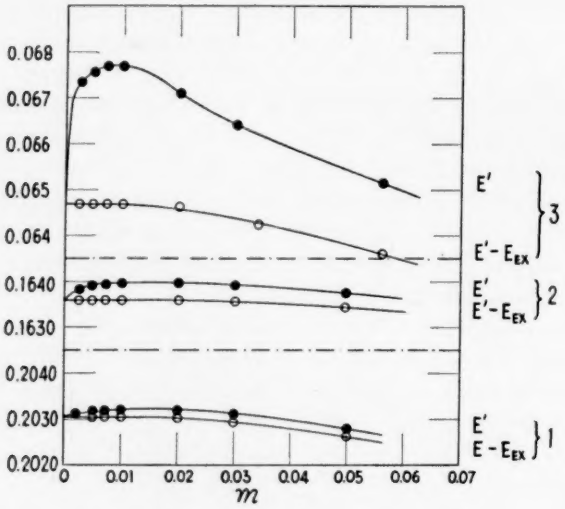
where E is the electromotive force of the cell, k equals 2.3026 R/TF, u is the universal isothermal constant of the Debye and Hückel theory, c the concentration in mols per 1000 cc. solution, A the parameter of the theory which involves the mean distance of approach of the ions "a," G_0, the mean molecular weight of the solvent (47) and E_0' the standard potential. It has been shown by Gronwall, LaMer, and Sandved (15) that the third term of this function as given by Debye and Hückel is a first approximation and that a more complete development of the theory involves "extended terms." This correction is very small with uniunivalent electrolytes in media of high dielectric constant. Since the correction varies inversely as the cube of the dielectric constant D, it cannot be neglected in media of low dielectric constant.

We have carried out the extrapolation by first using a preliminary value of "a" ($\sim$ 5 Ångstroms). From this value of "a," we computed the extended term correction from Table V of their contribution. This quantity was multiplied by $2k$ to convert to volts, and the value obtained designated E_{Ex}. The function E' and $E' - E_{Ex}$ were plotted against m, and if $(E' - E_{Ex})$ was not constant at low concentrations (< 0.02 M), another value of "a" was employed. This process was repeated until such constancy was obtained.

Three such graphs for the cases of the 20 per cent., 45 per cent., and 70 per cent. dioxane solutions are shown in Fig. 11. These are drawn on the same electromotive force scale. The upper curves of each pair represents the plots of E' and the lower those of $E' - E_{Ex}$. All the graphs of E' show "the characteristic hump" predicted by theory. The magnitude of the hump increases very rapidly $\left(\propto \frac{1}{D^3} \right)$ with decreasing

dielectric constant. The values $(E' - E_{Ex})$ are constant at concentrations below 0.01 to 0.02 N. The values of "a" employed were 6.1, 5.4, and 5.0 Ångstroms in the cases of the 70, 45, and 20 per cent. solutions, respectively. This may be interpreted as being caused by the formation of larger ionic complexes with solvent in the media containing the larger number of dioxane molecules. Similar extrapolations from 0° to 50° indicate that "a" decreases with temperature which fact also indicates the breaking up of larger ionic complexes at the higher temperatures.

FIG. 11.



Standard Potential Extrapolations in Dioxane-Water Mixtures at 25°.

1. 20 per cent. Dioxane (D = 60.8).
2. 45 per cent. Dioxane (D = 38.5).
3. 70 per cent. Dioxane (D = 17.7).

The curve for the 70% dioxane solutions was constructed from the data of Harned and Morrison and is not altogether satisfactory since the lowest concentration was 0.003 M. More results at still lower concentrations have been obtained recently by Mr. C. Calmon in our laboratory and a preliminary plot of them indicates that the graph in Fig. 11 is correct to within very narrow limits.

PART IV.

EXTRAPOLATION TO SATURATED SOLUTIONS AND THE CALCULATION OF THE SOLUBILITY OF HIGHLY SOLUBLE SALTS IN SALT SOLUTIONS BY THE METHOD OF ÅKERLÖF.

We have emphasized the importance of the extrapolation of results to zero concentration. To complete the discussion, we shall describe methods of extrapolation of activity coefficients to saturated solutions, and show how such a procedure leads to a method of calculation of the solubility of highly soluble salts in salt solutions.

Since the reference state for solubility is the solid salt, we may write for the thermodynamic solubility product, P_s, the expression,

$$P_s = a_1^{+\nu_1^+} a_1^{-\nu_1^-} = (m_+)^{\nu_1^+} (m_-)^{\nu_1^-} \gamma_1^{+\nu_1^+} \gamma_1^{-\nu_1^-}, \quad (24)$$

where a_1^+, a_1^-, γ_1^+, γ_1^- are the activities and activity coefficients of the cations and anions of the saturating salt, ν_1^+, ν_1^-, the number of cations and anions obtained from the dissociation of one molecule of salt (e.g. NaCl; $\nu_1^+ = 1$, $\nu_1^- = 1$; $BaCl_2$, $\nu_1^+ = 1$; $\nu_1^- = 2$), and m_+ and m_- are the molalities of the anion and cation of the saturating salt. This equation is simpler to employ in the logarithmic form, or

$$\frac{1}{\nu_1^+ + \nu_1^-} \log P_s = \frac{1}{\nu_1^+ + \nu_1^-} \log m_+^{\nu_1^+} m_-^{\nu_1^-} + \log \gamma_1. \quad (25)$$

For a single electrolyte, all quantities of this equation are known if γ_1 can be extrapolated to the saturated solution where the molality is $m = \frac{m_+}{\nu^+} = \frac{m_-}{\nu^-}$.

A very convenient extrapolation function which is valid in concentrated solutions of electrolytes has been employed by Åkerlöf (5) (2) (3) (6). This is,

$$\log \frac{\gamma_1}{\gamma_R} = B_{RI}\mu, \quad (26)$$

where γ_R is the activity coefficient of a reference electrolyte, B_{RI} is a constant, and μ the ionic strength. Åkerlöf has employed hydrochloric acid as the reference electrolyte. By

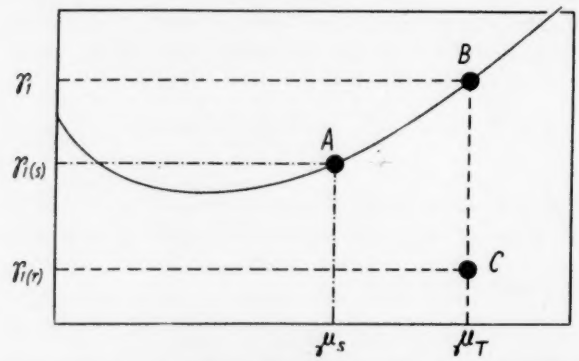
combining relations (25) and (26),

$$\frac{1}{\nu_1^+ + \nu_1^-} \log P_s = \frac{1}{\nu_1^+ + \nu_1^-} \log \nu_1^{+\nu_1^+} \nu_1^{-\nu_1^-} + \log \frac{\mu_s}{f'} + \log \gamma_{R(\mu s)} + B_{RI}\mu_s \quad (27)$$

is obtained. f' is a factor which converts the molality to the ionic strength. Knowing B_{RI} for the saturating salt, the isothermally constant left side of this equation may be evaluated readily.

Upon addition of a second salt, the various quantities on the right of this equation vary while the whole expression remains constant. In order to determine the solubility, it is necessary to know γ_1 of the saturating salt in the salt solution. The addition of salt causes a change in total ionic strength, μ_T, and in ionic strength of saturating salt. These changes are shown in Fig. 12 where γ_1 is plotted against μ. At A the

FIG. 12.



Illustrating the Variation of the Activity Coefficient as a Function of Ionic Strength in a Solution of a Second Electrolyte.

saturating salt possesses an activity coefficient $\gamma_{1(s)}$ and an ionic strength μ_s. In the salt solution, its activity coefficient is $\gamma_{1(T)}$ at an ionic strength of μ_T. Åkerlöf assumes that the change from A to B is given by equation (26). To obtain the change from B to C, he makes use of the empirical approximation of the linear variation of the logarithm of the

activity coefficient of an electrolyte in a mixture at constant total ionic strength. This may be formulated as follows:

$$\begin{aligned} \log \gamma_1 &= \log \gamma_{1(0)} - \alpha_{12}\mu_2, \\ \log \gamma_2 &= \log \gamma_{2(0)} - \alpha_{21}\mu_1. \end{aligned} \tag{28}$$

In the mixture of two electrolytes, γ_1, γ_2 are the activity coefficients, μ_1 and μ_2 their ionic strengths, $\mu_T = \mu_1 + \mu_2$, $\gamma_{1(0)}$ is the activity coefficient of the first electrolyte when $\mu_2 = 0$, $\gamma_{2(0)}$ the activity coefficient of the second electrolyte when $\mu_1 = 0$, and α_{12} and α_{21} are constants. By the linear combination of the relations given by equations (26) and (28), $\gamma_{1(T)}$ the activity coefficient of the saturating salt in the presence of the co-solute may be determined and, subsequently, the solubility μ_X.

For the present purpose, it will suffice to write the equation for the simple case of the heterionic solution in which none of the ions of saturating salt are common with those of the co-solute. This equation is,

$$\begin{aligned} C = \log \mu_s + \log \gamma_{R(\mu_s)} + B_{RI}\mu_s = \log \mu_X + \log \gamma_{R(\mu T)} \\ + B_{RI}\mu_T + \alpha_{21}(\mu_T - \mu_X), \end{aligned} \tag{29}$$

where C is an isothermal constant. The homoionic cases although more complicated algebraically requires no more experimental constants and will not be required in this explanation of the method. In this equation, μ_s is the solubility of the saturating salt in the solvent containing no co-solute. Since the activity coefficient of the reference electrolyte, $\gamma_{R(\mu_s)}$ is known, and B_{RI} previously determined, a single measurement of solubility in pure solvent permits the evaluation of the constant left side of the equation. Further, the second and third term on the right are known also. Therefore, if the constant, α_{21}, is known, then μ_x, the solubility of saturating salt in the mixture at any total ionic strength, μ_T, may be computed, providing that $\alpha_{21} \neq f(m)$.

There are three possibilities of employing equation (29) for the computation of solubility data.

(1) If no previous knowledge is available concerning the activity coefficient of the saturating salt or its behavior in the mixtures, at least three determinations of the solubility, one

of which is in the absence of the co-solute, are necessary in order to evaluate the parameters, C, B_{RI} and α_{21}.

(2) If the activity coefficient of the saturating salt is known in solution in the pure solvent at high concentrations, B_{RI} is known, and, therefore, only the solubility in the pure solvent, and one solubility in the salt solution is required for the determination of α_{21}. This information is frequently available, and represents the usual case.

(3) The most interesting case is that in which sufficient data are available in the unsaturated solutions so that both B_{RI} and α_{21} are known. Then, from a single determination of the solubility in pure solvent the solubility in the co-solute solutions at all concentrations may be determined. One striking example of this case is the solubility of sodium chloride in hydrochloric acid solutions. From electromotive force measurements (21), (46) the activity coefficient of hydrochloric acid in sodium chloride solutions has been determined. From these α_{12} has been computed and found to remain constant with increasing molality at high concentrations ($> 2M$) (21). From these, and B_{RI}, α_{21}, the slope of the curve of the logarithm of the activity coefficient of sodium chloride in hydrochloric acid solutions, has been computed by the use of the Gibbs-Duhem equation. α_{21} was also found to be independent of μ when $\mu > 2M$. From μ_s the solubility of sodium chloride in pure water at 25°, and these values of α_{21} and B_{RI}, the solubility of sodium chloride in hydrochloric acid solutions, μ_X, has been computed up to a total molality of 14. These calculated results agree with observed solubilities to within $\pm$ 0.1%.

Åkerlöf has applied this equation to over fifty cases of solubilities of salts in salt solutions, and obtained excellent agreement with the observed results in all cases where the solubility data could be relied on. Of these we may mention such varied cases as sodium chloride in sodium nitrate, cuprous chloride in potassium chloride, barium nitrate in aluminum nitrate and thorium nitrate, and potassium ferricyanide in potassium chloride solutions in which cases the equation fits the experimental results to within $\pm$ 0.5 per cent. A further extension permits the calculation of the composition of the liquid phase in such systems as sodium sulphate-sodium

chloride-water at 25° in the presence of sodium chloride, anhydrous sodium sulphate, and sodium sulphate decahydrate as solid phases (3).

These illustrations are sufficient to show the value of extrapolation of activity coefficients to saturated solutions. Beside the practical value of such calculations, the measurements serve as an excellent check on the validity of experimental studies of mixtures of electrolytes in the liquid phases at the higher concentrations.

SUMMARY.

We have surveyed in a brief manner some phases of the experimental thermodynamics of electrolytic solutions. A more complete review would be very voluminous, and would include a number of other topics. As examples, the investigations of electrolytes of higher valences types such as cadmium chloride (34), and iodide (8), barium chloride (85), and zinc sulphate (11) (55). It would also include a discussion of the important work of Gibson (14) who has measured the compressions of a number of aqueous salt solutions up to 1000 bars. Nor have we discussed the recent interpretations of the behaviors of strong electrolytes in solutions at higher concentrations where the theory of Debye and Hückel is no longer adequate without considerable extension. This complicated subject has been investigated most comprehensively by Scatchard (78) (80) and its discussion would lead beyond the intended limits of this survey. We trust that this sketch of our results will help somewhat to give a correct impression of the extent and direction of this part of solution chemistry. The development of method in these studies of equilibria has reached the stage where a really reliable and accurate body of evidence is becoming available. This is very important because accurate data will be required not only as criteria and as a guide to the approximate statistical and quantum mechanical interpretations of equilibrium constants, entropies, activation energies, and reaction velocity constants where ions are involved, but also in the further clarification of the state of ions in solution.

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Cupaloy—A New Alloy with High Strength and High Conductivity.—P. H. BRACE (*The Electric Journal*, Vol. 36, No. 3). Those engaged in the development of the electrical industry have on many occasions felt keenly the need for an alloy having the electrical and thermal properties of copper together with the hardness and strength of steel. Research metallurgists have sought the solution of this difficulty and, have developed a material known as Cupaloy. Actually it is very nearly 99.44/100 per cent. pure copper. The principal alloying ingredients are chromium (itself a product of modern electrotechnology) and silver. It differs fundamentally from the older hard alloys of copper because of the peculiar associations of the ingredients and the resulting combination of hardness with high thermal and electrical conductivity. Chromium has been caused to form billions of tiny crystallites distributed quite uniformly throughout the mass of the metal by means of appropriate heat treatments. Although these crystallites are too small to be seen even with the microscope there are many reasons for assuming their existence. Cupaloy has a great deal of ductility and may be further hardened and strengthened by cold working in any one of various ways such as hammering, cold rolling, or drawing through dies. By such means the elastic strength of temper hardened Cupaloy can be brought up to 35,000 pounds per square inch or more with corresponding increase in hardness and but little impairment of thermal and electrical conductivity. In this new alloy the electrical and thermal conductivities may exceed 85 per cent. of those of pure copper. Another valuable property is its stability at elevated temperatures. Prolonged heating at temperatures up to 400 deg. C. causes relatively little permanent softening of Cupaloy as produced. Many applications are open to this new and unique material.

R. H. O.

THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF ELECTROLYTES.

BY

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Water is, of course, the most important solvent with which we have to deal. An understanding of aqueous solutions is a prime necessity to both the animal and plant physiologist. Such solutions play a dominant rôle in the studies of the geologist, the soil physicist, and the oceanographer.

From a theoretical point of view water is also particularly interesting. With unimportant exceptions, it is the solvent having the highest dielectric constant. In studying aqueous solutions we are observing one extreme of behavior. It has been known for a very long time that water is an excellent solvent for salts and that the resulting solutions are highly conducting. It is with no apology, therefore, that I limit my contribution to the discussion in this symposium to aqueous solutions of salts, acids, and bases.

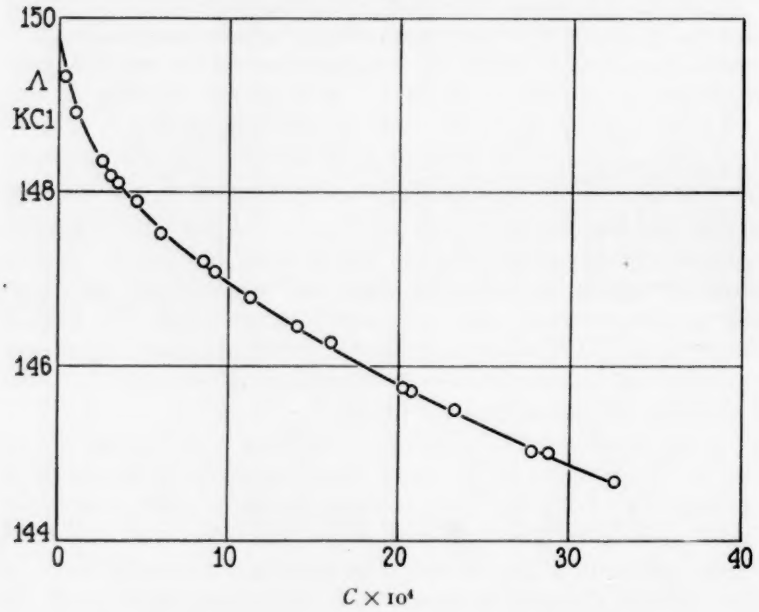
If the equivalent conductance Λ of a salt, potassium chloride, for example, is plotted as a function of the concentration the result is a curve such as is shown in Fig. 1. As is certainly quite familiar to this audience, Arrhenius, Ostwald, and their school attributed the decrease in equivalent conductance as the concentration is increased to a decreasing number of the carriers of electricity, i.e., the ions. In doing so they made the assumption that ions neither speed up nor slow down, relatively, when the concentration is changed. Much of the content of the theory is stated by Arrhenius' equation

$$\alpha = \frac{\Lambda_C}{\Lambda_0}, \qquad (1)$$

in which α is the "degree of dissociation," in other words, the proportion of the salt present as ions, and Λ_C and Λ_0 are respectively the equivalent conductance at the concentration C,

and at infinite dilution. The range and limits of agreement of this theory with the results of experiment are an old story to those of us who studied chemistry a generation ago. There was sufficient accord to be reasonably convincing between observation and theory for the thermodynamic properties of salt solutions, and for the conductances of solutions of at least "weak" acids and bases. However, there always remained what was called "the anomaly of the strong electrolyte." No

FIG. 1.



amount of finagling by the proponents of the Arrhenius theory could make the results of the conductance measurements on solutions of "strong" acids, bases, and salts fit the law of mass action, which, with the assumptions then current, yielded the relation known as "Ostwald's dilution law" which is

$$\mathbf{K} = \frac{C\alpha^2}{(1 - \alpha)}, \qquad (2)$$

in which **K** is the ionization constant. A number of investiga-

tors, including A. A. Noyes and G. N. Lewis, viewing the repeated failures of the theory, became bold enough to question the validity of equation (1) and to suggest that strong electrolytes are more highly dissociated than that equation would imply. Their conclusions were largely based upon the additivity of such properties as color and optical activity. Another point of attack on the theory was a theoretical one. To Sutherland and others it appeared strange that the highly charged ions should exist so closely to each other as they do in a solution without interionic influences brought about by electrostatic attractions and repulsions. The unsuccessful attempt by Ghosh to account for the conductances of strong electrolytes by the interplay of electrostatic forces and thermal vibrations had at least the historic importance of directing the attention of Debye and Hückel to the same task. The great accomplishment of these authors in connection with the thermodynamic properties of solutions of electrolytes is discussed in this symposium by Professor Harned. The most important conclusion of Debye and Hückel, for my present purpose, was that the properties of solutions of strong electrolytes can be most readily accounted for if these substances are assumed to be completely dissociated in aqueous solutions. The change of the equivalent conductances of strong electrolytes with the concentration, exemplified by Fig. 1, had therefore to be sought in some other explanation than a variation of the number of ions with the concentration. For this purpose Debye and Hückel drew upon two "effects" both of which would decrease the mobilities, i.e., slow up the ions, as the number of ions in solution increased. These are (*a*) the electrophoretic effect, and (*b*) the time of relaxation effect. Although these authors made a great contribution to the theory of conductance of electrolytes, the most recent and successful form of the theory is largely due to Onsager. The *electrophoretic effect* and the *time of relaxation effect* will be discussed, as far as space permits, in the order given.

THE ELECTROPHORETIC EFFECT.

As already mentioned during this symposium, according to the Debye-Hückel theory an ion is surrounded by an "ionic atmosphere" distributed with radial symmetry around the

ion as center. This ion atmosphere, it will be recalled, is due to the fact that interionic attractions and repulsions tend to produce a slight preponderance of negative ions in the vicinity of a positive ion and *vice versa*. Although the ion atmosphere is treated as a reality in mathematical discussions it actually is the result of a time average of a distribution of the ions. Each ion serves as a center of an ion atmosphere, and the relative position of each ion with respect to the other charged bodies in the solution influences the atmospheres of all the other ions.

One result of the presence of an ionic atmosphere is that there is a potential field distributed with radial symmetry around an ion, the value of the potential, ψ, being given by the formula

$$\psi = \frac{z_i \epsilon}{D} \frac{e^{\kappa a_i}}{1 + \kappa a_i} \cdot \frac{e^{-\kappa r}}{r}, \tag{3}$$

in which ϵ is the charge on a proton, z_i is the valence of an ion species i, and a_i is the "distance of closest approach" of a pair of ions. D is the dielectric constant, r is the radial distance from the center of the ion, and κ, an important quantity in the Debye-Hückel theory, has the dimension of a reciprocal length and is a function of the ion concentration. From this equation and Poisson's relation

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \frac{4\pi}{D} \rho \tag{4}$$

the corresponding distribution of the space charge, ρ, in the ion atmosphere as a function of the distance, r, may be obtained by eliminating ψ between equations (3) and (4). The resulting expression is

$$\rho = -\frac{z_i \epsilon e^{\kappa a_i}}{4\pi(1 + \kappa a_i)} \kappa^2 \frac{e^{-\kappa r}}{r}. \tag{5}$$

If a potential gradient of intensity E is impressed on the solution a selected ion will move with a velocity that will be denoted by v_i. This velocity is independent of the presence of other ions, and is determined by the limiting conductance λ_0 of the ion constituent. The ion atmosphere, however, being of opposite charge to the ion itself will tend to move in a

reverse direction. Each element of the ion atmosphere will be acted on by a force F, per unit volume, given by the relation

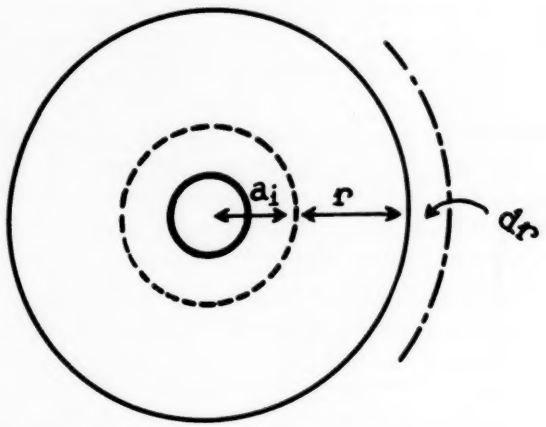
$$F = \rho E, \tag{6}$$

which with equation (5) gives

$$F = -E\frac{z_i\epsilon e^{\kappa a_i}}{4\pi(1+\kappa a_i)}\kappa^2\frac{e^{-\kappa r}}{r} = -A\frac{e^{-\kappa r}}{r}, \tag{7}$$

in which A is a constant for a given solution and potential gradient. Around the selected ion the atmosphere may be considered to be arranged, as is shown in Fig. 2, in spherical

FIG. 2.



shells of thickness, dr, in each of which the force per unit volume F is constant. The force dF acting on such a shell will be

$$dF = 4\pi r^2 F dr. \tag{8}$$

As a result of this force the shell and contents, including the ion, will tend to move with a velocity dv_2 in a direction contrary to the motion of the ion.

The velocity of a sphere of radius r in a fluid of viscosity, η, moving under a force F, is given by Stokes' law

$$v = \frac{F}{6\pi\eta r}. \tag{9}$$

From equations (7), (8), and (9), therefore, the contribution, dv_2, of a spherical shell of thickness, dr, to the velocity v_2 will be

$$dv_2 = -\frac{2A}{3\eta} e^{-\kappa r} dr. \qquad (10)$$

Integrating this expression between the distance of closest approach a_i and infinity and substituting the value of A from equation (7) yields

$$v_2 = -\frac{E\epsilon z_i}{6\pi\eta} \frac{\kappa}{1 + \kappa a_i}. \qquad (11)$$

The resultant velocity of the ion will be, for solutions dilute enough so that κa_i is small compared with unity

$$v = v_1 + v_2 = v_1 - \frac{E\epsilon z_i \kappa}{6\pi\eta}. \qquad (12)$$

The factors determining the velocity v_1 are, so far, unknown. The velocity, v_1, however, determines the limiting conductance, λ_0, of an ion. The velocity v_2, which has an opposite sign to that of v_1, is the retardation due to the electrophoretic effect. In the case of potassium chloride, for instance, the electrophoretic effect accounts for the greater part of the decrease of the equivalent conductance with the increase of concentration.

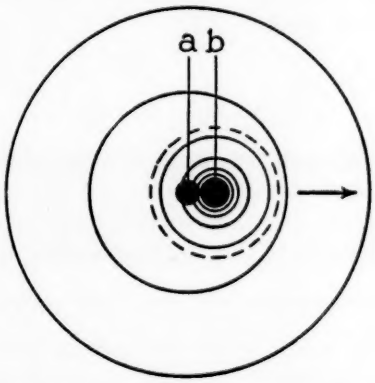
It has been customary to deal with the ionic atmosphere as if it were a reality, and the derivation just given assumes that an electric force acting on the ion atmosphere will produce a motion of the solvent. However, the effect of a potential gradient cannot be directly on the solvent, but must have its influence indirectly through the ions. The fundamental explanation of the electrophoretic effect must therefore be sought in a modification of inter-reactions between ions and solvent produced by the ion atmosphere, and the latter is, as we have seen, due in turn to a time average of the distribution of the ions.

THE TIME OF RELAXATION EFFECT.

The other mechanism tending to decrease the equivalent conductance of an electrolyte when the ion concentration is

increased is, as already mentioned, the "time of relaxation effect." The underlying assumptions made in deriving an expression for the effect are as follows. Around a selected ion the atmosphere has spherical symmetry. If the ion is suddenly moved the ion atmosphere will tend to move with it. The adjustment of the ion atmosphere to the new condition will take place rapidly, but, however, not instantaneously. An attempt to provide a picture of the effect is given in Fig. 3.

FIG. 3.



If an ion, initially at the point *a* is suddenly moved to the point *b* the ion atmosphere, originally symmetrical about position *a*, tends to rearrange itself to be symmetrical about *b*. In the figure the part inside the dotted circle has adjusted to the new position of the ion, but the point outside that circle is asymmetrically arranged with respect to the ion. The result is that the adjusted portion of the atmosphere tends to exert an electrostatic attraction in a contrary direction to the motion of the ion, which is represented as being in the direction of the arrow. If an ion is moving steadily the ion atmosphere will be under the influence of a permanent distortion the effect of which is to decrease the velocity of the ion under a given external force. The effect, being purely electrostatic, is independent of the viscosity of the medium. It does, however, depend upon the limiting conductance, λ_0, of the ion constituent. A derivation of the relations is a quite elaborate problem in statistical mechanics for which the reader is re-

ferred to the articles by Onsager.[1] His equation for the equivalent conductance, λ, of an ion constituent which has a valence z_i for a solution containing C equivalents of solute per liter is

$$\lambda = \lambda_0 - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} w\lambda_0 + \frac{28.94 z_i}{(DT)^{1/2}\eta} \right] \sqrt{(z^+ + z^-)C}, \quad (13)$$

in which z^+ and z^- represent respectively the valence of the positive and negative ion constituents. D and η are the dielectric constant and the viscosity of the solvent, and T is the absolute temperature. Also

$$w = z^+ z^- \frac{2q}{1 + \sqrt{q}}; \quad q = \frac{z^+ z^- (\lambda_0^+ + \lambda_0^-)}{(z^+ + z^-)(z^+ \lambda_0^- + z^- \lambda_0^+)}, \quad (14)$$

in which λ_0^+ and λ_0^- are the limiting equivalent conductances of the positive and negative ions. The first term in the brackets in equation (13) accounts for the time of relaxation effect and the second for the electrophoretic effect.

THE VALIDITY OF ONSAGER'S EQUATION FOR AQUEOUS SOLUTIONS.

It is, of course, important to determine with what accuracy and within what range of concentration Onsager's equation, represented by the expression (13) is confirmed by the results of experiments. It will be well to recall that the equation refers to the *ionic part only* of a dissolved electrolyte. For a univalent ion, equation (13) takes the form

$$\lambda = \lambda_0 - \left[\frac{8.147 \times 10^5}{(DT)^{3/2}} \lambda_0 + \frac{40.93}{(DT)^{1/2}\eta} \right] \sqrt{C}, \quad (15)$$

which for a given solvent medium and temperature may be put in the form

$$\lambda = \lambda_0 - [\vartheta\lambda_0 + \tfrac{1}{2}\sigma]\sqrt{C}, \quad (16)$$

in which ϑ and σ are constants. Thus the expression connecting the concentration C with the equivalent conductance, Λ, of a uni-univalent electrolyte, for which

$$\Lambda = \lambda^+ + \lambda^-$$

[1] L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

is

$$\Lambda = \Lambda_0 - [\vartheta\Lambda_0 + \sigma]\sqrt{C}. \qquad (17)$$

For aqueous solutions at 25° the constants of equation (17) have the values $\vartheta = 0.2273$ and $\sigma = 59.78$.

In the derivation of equation (13) a number of simplifying assumptions of a physical nature, and mathematical approximations, such as taking only the first terms of a series, were made. The expressions are therefore strictly valid only as limiting equations and may be expected to hold only for very dilute solutions. It is of interest that Kohlrausch observed, empirically, that the conductances of dilute strong electrolytes follow the relation

$$\Lambda = \Lambda_0 - K\sqrt{C}, \qquad (18)$$

in which K is a constant. Onsager's equation (13) leads to an expression of this form but also predicts, for each electrolyte, the value of the constant K. Onsager showed, mainly from Kohlrausch's data, that equation (17) is the limiting relation between Λ and the concentration C for strong electrolytes.

The most recent and accurate test of the equation is, however, due to Shedlovsky,[2] who was able to make measurements of conductances with precision at concentrations as low as 0.00003 normal. The range of the agreement between the theory and the measurements is shown in Fig. 4, based on Shedlovsky's investigations, in which the equivalent conductance, Λ, of a number of typical uni-univalent strong electrolytes is plotted with the square root of the concentration as abscissae. A plot of Onsager's equation is also shown, for each electrolyte, as a straight line with a slope equal to $(\vartheta\Lambda_0 + \sigma)$. It is evident that in each case this line clearly represents the observations, within the small experimental error, up to a concentration of about 0.001 mole per liter, above which concentration there is, in most cases, a slight but definite upward deviation.

A further important test of Onsager's expression, equation (13), is of its validity when used with conductance data on salts of the higher valence types. For aqueous solutions of a bi-univalent electrolyte, such as calcium chloride at 25°, this

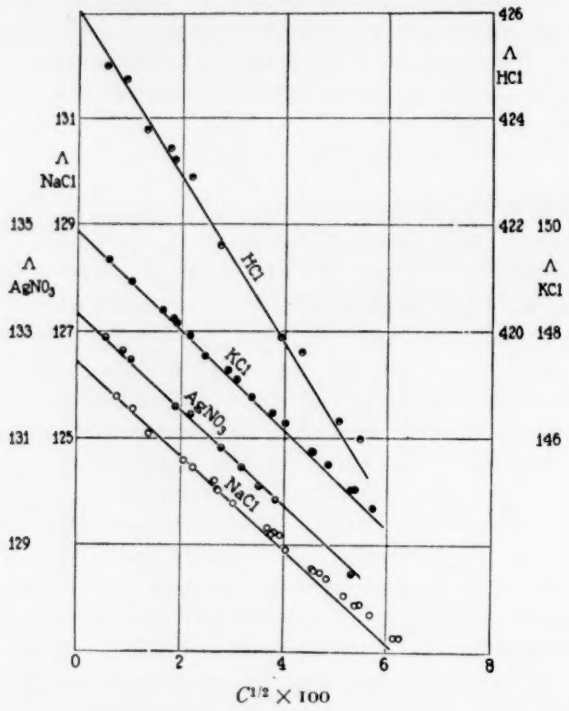
[2] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

equation may be readily seen to reduce to

$$\Lambda = \Lambda_0 - \left(\frac{1.2673\,\Lambda_0}{1 + t_0^- + 0.8165\sqrt{1 + t_0^-}} + 109.819 \right) \sqrt{C}, \quad (19)$$

in which the limiting transference number, t_0^- is, equal to the ratio λ_0^-/Λ_0 and C is the concentration in equivalents per

FIG. 4.



liter. For a salt of tri-univalent type, such as lanthanum chloride, the corresponding equation is

$$\Lambda = \Lambda_0 - \left(\frac{9.0}{1 + 2t_0^- + 0.8660\sqrt{1 + 2t_0^-}}\Lambda_0 + 169.08 \right) \sqrt{C}. \quad (20)$$

The method for obtaining the limiting transference numbers, t_0^-, will be indicated later in this paper. For calcium and lanthanum chlorides at 25° equations (19) and (20) become

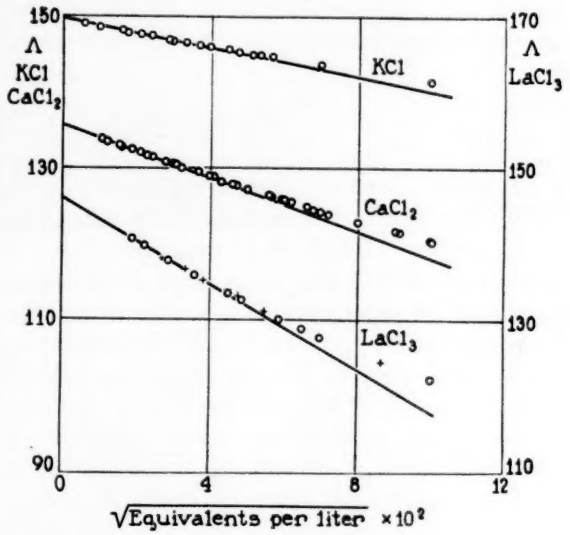
respectively

$$\Lambda = \Lambda_0 - (0.49073 + 109.82)\sqrt{C}, \qquad (21)$$

$$\Lambda = \Lambda_0 - (0.75131 + 169.08)\sqrt{C}. \qquad (22)$$

In Fig. 5 the results of recent determinations of the equivalent conductance, Λ,[3, 4, 5, 6] of the three different valence types are plotted as functions of the square root of the equivalent concentration and, for comparison, the straight lines representing the corresponding Onsager equations. It will be observed

FIG. 5.



that the equation in each of these cases accurately represents the data for the more dilute solutions.

The evidence just given, which is typical of that obtained from all recent measurements, shows that the Onsager equation is valid for very dilute aqueous solutions of strong electrolytes. This fact is important as it lends strong support to the correctness and utility of the interionic attraction theory.

[3] T. Shedlovsky, A. S. Brown, and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[4] T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.*, **56**, 1066 (1934).

[5] G. Jones and C. F. Bickford, *ibid.*, **56**, 602 (1934).

[6] T. Shedlovsky, private communication.

As has already been emphasized, Onsager's equation is a limiting equation and deviations from it, even for completely dissociated electrolytes, are to be expected as the concentration is increased.

EVIDENCE FROM TRANSFERENCE NUMBERS FOR THE CORRECTNESS OF THE ONSAGER EQUATION.

An important and quite sensitive test of the validity of the Onsager equation, and of the ideas underlying it, is afforded by transference number measurements. It will be recalled that the Arrhenius theory of ionization assumed that ions have the same mobilities at all concentrations. The transference number, t^+, of the cation constituent of a binary electrolyte is equal to

$$t^+ = \frac{\lambda^+}{\lambda^+ + \lambda^-}, \tag{23}$$

in which λ^+ and λ^- are the ion constituent conductances. Thus if mobilities are independent of the concentration the transference number must be constant also. However, transference numbers are not constant, but change with concentration, a fact which, in itself, is sufficient to throw doubt on the Arrhenius theory. The interionic attraction theory, on the other hand, requires decreases of ion mobilities with increasing ion concentrations. This leads, as the following discussion will show, to changes in the transference number with concentration, even for very dilute salt solutions. With the aid of equation (16), equation (23) may be put in the form

$$t^+ = \frac{\lambda_0^+ - (\vartheta\lambda_0^+ + \frac{1}{2}\sigma)\sqrt{C}}{\lambda_0^+ + \lambda_0^- - [\vartheta(\lambda_0^+ + \lambda_0^-) + \sigma]\sqrt{C}}. \tag{24}$$

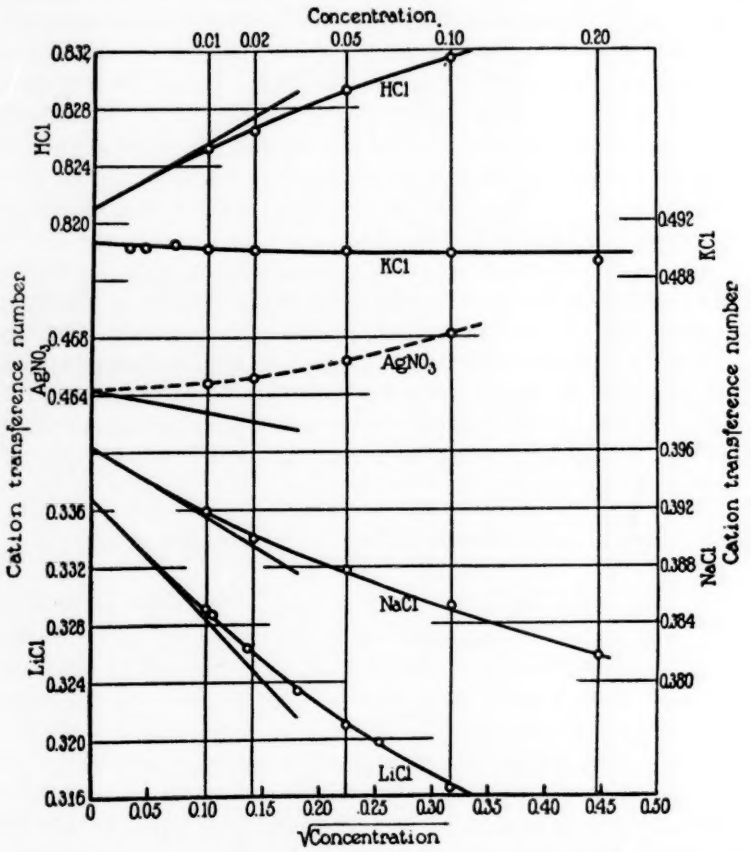
This equation shows that even for solutions dilute enough for the Onsager equation to hold the transference numbers should, in general, change with the concentration, if the interionic attraction theory is valid.

By differentiating equation (24) with respect to $\sqrt{C}$, and including the condition that C approaches zero, the expression

$$\left(\frac{dt}{d\sqrt{C}}\right)_{C\to 0} = \frac{t_0^+ - 0.5}{\Lambda_0}\sigma \tag{25}$$

is obtained, in which $t_0^+ = \lambda_0^+/(\lambda_0^+ + \lambda_0^-)$. It follows therefore that a plot of transference numbers of univalent electrolytes against $\sqrt{C}$ should enter the axis of zero concentration with a slope given by equation (25). The limiting slope

FIG. 6.



should thus be proportional to the deviation of t_0^+ from 0.5 and inversely proportional to the limiting equivalent conductance, Λ_0, of the electrolyte.

A plot of transference numbers of uni-univalent electrolytes is shown in Fig. 6 and is based on the data of Longsworth,[7]

[7] L. G. Longsworth, *J. Am. Chem. Soc.*, **57**, 1185 (1935).

who, utilizing the "method of moving boundaries," was able to achieve a high order of accuracy. The scale of ordinates in the figure is the same for all the electrolytes but the ordinates themselves have been shifted to make the plot more compact. The circles represent the experimental results and the smooth curves have been drawn through them to the limiting value t_0^+ of the transference number, obtained as will be shortly described. The straight line starting from t_0^+ has in each case the limiting slope given by equation (25). It will be seen that for the four chlorides the curve through the experimental points evidently merges into the line having the limiting slope. Thus for these substances the interionic attraction theory predicts the sign and, for very dilute solutions, the magnitude of the change of the transference number with the concentration.

The transference numbers of certain electrolytes, however, show variations from the predictions of the theory. The data for silver nitrate are plotted in Fig. 6 and it is seen that the variation of the transference number of that substance with concentration is in the opposite direction from that required by the theory. In general, however, the transference data lend strong support to the interionic attraction theory of electrolytic conductance.

EMPIRICAL EXTENSIONS OF THE ONSAGER EQUATION TO HIGHER CONCENTRATIONS.

As has been explained, the Onsager equation is strictly valid only as a limiting expression. In the derivation of the equation higher terms in mathematical series were neglected, also such complications as interactions between the electrophoretic and time of relaxation effects were not considered. Onsager [1] found that agreement with the experimental data on conductance measurements can be extended to somewhat higher concentrations than with the limiting equation by the use of the modified formula

$$\Lambda = \Lambda_0 - (\vartheta\Lambda_0 + \sigma)\sqrt{C} + bC, \qquad (26)$$

in which b is an empirical constant. A more useful equation has, however, been suggested by Shedlovsky [8] who observed that for most strong uni-univalent electrolytes values of Λ_0'

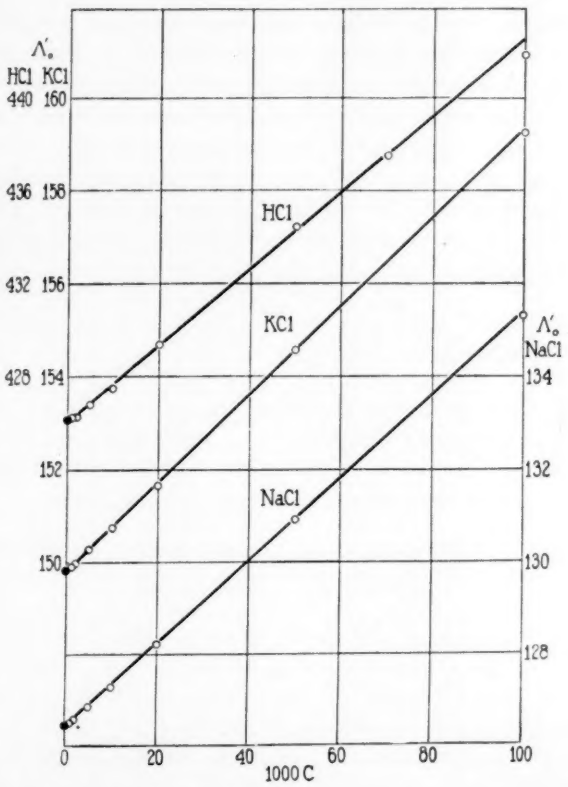
[8] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).

computed from the Onsager equation in the form

$$\Lambda_0' = \frac{\Lambda + \sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} \qquad (27)$$

are linear with respect to the concentration C. In the concentration region in which Onsager's equation holds Λ_0' is

FIG. 7.



obviously equal to Λ_0. Under other conditions Λ_0' varies with C. A plot of Λ_0' values for solutions of sodium and potassium chlorides and hydrochloric acid as ordinates against the concentration C is shown in Fig. 7 and is based on Shedlovsky's data. It is evident that the plots for these substances are, very nearly at least, straight lines. Shedlovsky's observation

may be put in the form of the equation

$$\frac{\Lambda + \sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} = \Lambda_0 + BC, \qquad (28)$$

in which B is an empirical constant.

For the conductance of solutions of the greater number of the strong uni-univalent electrolytes equation (28) expresses the data very nearly within the experimental error. It does not, however, serve for the data on nitrates and chlorates. We have already seen that silver nitrate is abnormal with respect to the relation of transference numbers to the concentration. Furthermore the conductance data on solutions of higher valence type, such as calcium chloride, lanthanum chloride, or sodium sulphate, show pronounced deviations from linearity when plotted as is shown in Fig. 7. In certain cases the data can be accurately expressed by the addition of terms to equation (28), giving

$$\frac{\Lambda + \sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} = \Lambda_0 + BC + DC \log C - EC^2. \qquad (29)$$

Although this equation is empirical it reduces to Onsager's equation for very small values of C, and the terms BC and $DC \log C$ are of the form required by consideration of factors neglected in the derivation of the simple equation.[9]

THE LIMITING CONDUCTANCE, Λ_0, OF AQUEOUS SOLUTIONS OF ELECTROLYTES AND THE LIMITING EQUIVALENT CONDUCTANCES, λ_0, OF THE ION CONSTITUENTS.

Since the value of the limiting equivalent conductance, Λ_0, was used in the computation of the degree of dissociation, α, according to the theory of Arrhenius, methods for obtaining that constant were considered from the early days of the ionic theory. In spite of the fact that the simple Arrhenius theory can no longer be considered valid the evaluation of Λ_0 retains interest as it is, as we have just seen, an important constant in Onsager's equation. The more recent methods for obtaining Λ_0 values are based on the assumption that the Onsager equation holds for very dilute solutions of strong electrolytes.

[9] L. Onsager, *Physik. Z.*, **28**, 277 (1927). L. Onsager and R. Fuoss, *J. Physic. Chem.*, **36**, 2689 (1932).

When accurate data on equivalent conductances are available at very low concentrations a simple graphical method for obtaining Λ_0 is, following Kohlrausch's early suggestion, to plot values of Λ as a function of the square root of the concentration and extend to the zero axis. The resulting line for strong electrolytes at concentrations below about 0.002 equivalent per liter has, in general, very nearly the slope required by the Onsager equation. Such a plot is shown in Fig. 4. A difficulty with the method just outlined is, however, that the greatest weight is given to the data obtained on very dilute solutions, where the experimental errors are greatest.

Another method, also dependent on the assumption that Onsager's equation is the true limiting relation, is based on the use of Shedlovsky's equation which for uni-univalent electrolytes takes the form

$$\frac{\Lambda + \sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} = \Lambda_0 + BC. \qquad (28)$$

The method of extrapolation consists in plotting values of Λ_0' defined by equation (27) against the concentration, C, and extending the line to the zero axis as shown in Fig. 7.

The equivalent conductance, λ^-, of the negative ion constituent of a binary electrolyte is defined as follows:

$$\lambda^- = t^-\Lambda, \qquad (30)$$

in which t^- is the anion transference number and Λ the equivalent conductance of the salt. If salts such as sodium and potassium chloride were completely dissociated and no interionic attraction existed the equivalent conductance of, for instance, the chloride ion constituent would be independent both of the concentration and of the nature of the positive ion with which it is associated. However, there is abundant evidence for interionic attractions so that λ values will be expected to change with concentration even in dilute solutions. Accurate conductance and transference data on solutions of chlorides are available for the study of the effect of the nature of the ion of opposite charge on the equivalent conductance of the chloride ion. From these data values of the product $\lambda_{Cl} = t_{Cl}\Lambda$ are given in Table I. It will be seen that the λ_{Cl}

TABLE I.

Equivalent Conductances of the Chloride Ion Constituent from Different Electrolytes at 25°.

Electrolyte.	Concentration, equivalents per liter.						
	0.001	0.002	0.005	0.01	0.02	0.05	0.10
KCl.....	74.88	74.28	73.22	72.07	70.56	68.03	65.79
NaCl.....	....	....	....	72.05	70.54	67.92	65.58
HCl.....	....	....	....	72.06	70.62	68.16	65.98
LiCl.....	....	....	....	72.02	70.52	67.96	65.49

values change markedly with the concentration. At 0.01 equivalent per liter, which is the lowest concentration for which there are data for more than one electrolyte the values of λ_{Cl} agree, almost within experimental error. At higher concentrations, however, these values show decided deviations, increasing as the concentration increases. The data tend to show that as the salt concentration is lowered the differences between the λ_{Cl} values from different salts tend to decrease and disappear completely in the limit. From these results, and others, it is a safe conclusion that at infinite dilution the equivalent conductance, λ_0, values are a property of the ion constituent alone and are independent of the associated ions. This is known as *Kohlrausch's law of the independent mobility of ions.*

A sensitive method for obtaining the limiting value of the conductance of chloride ion constituent, λ_{0Cl}, is shown in Fig. 8. Here values of λ'_{0Cl} defined by

$$\lambda'_{0Cl} = \frac{t_{Cl}\Lambda + \frac{1}{2}\sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} = \frac{\lambda + \frac{1}{2}\sigma\sqrt{C}}{1 - \vartheta\sqrt{C}} \qquad (31)$$

are plotted as functions of the concentration C. It will be seen that the curves through the points for each electrolyte are very nearly straight lines and that they converge to the same point on the zero axis. A graphical extrapolation leads to a value of

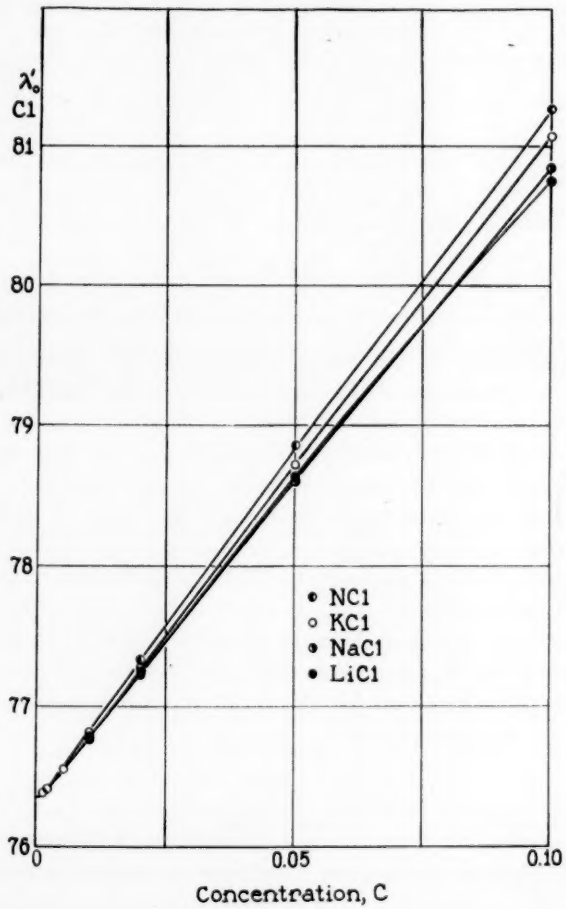
$$\lambda_{0Cl} = 76.34 \qquad (32)$$

for the limiting conductance of the chloride ion constituent, the greatest weight being given to the values of λ_{0Cl} from

potassium chloride since the measurements extend to very dilute solutions.

According to Kohlrausch's law, for which experimental evidence has just been given, the limiting equivalent conduc-

FIG. 8.



tances, Λ_0, of the salts are additive functions of the limiting ion conductances, λ_0. The values of λ_{0Cl} may be, therefore, used to obtain the limiting conductances of the cations of all chlorides for which Λ_0 values are available, and the values for

the cations may be, in turn, used to obtain the λ_0 values for other anions. The limiting ion conductances at 25° collected in Table II are based on conductance and transference meas-

TABLE II.

Limiting Ion Conductances at 25°.

Cation	λ_0^+	Anion	λ_0^-
K	73.52	Cl	76.34
Na	50.11	NO_3	71.44
H	349.82	CH_3OOO	40.9
Ag	61.92	Br	78.4
Li	38.69	I	76.8₅
NH_4	73.4	HCO_3	44.48
½Ca	59.50	½SO_4	79.8
½Ba	63.64	....	....
½Sr	59.46	....	....
½Mg	53.06	....	....
⅓La	69.6	....	....

urements made in the Rockefeller Institute laboratory. With this table it is possible to obtain by addition the limiting equivalent conductances of salts on which conductance data are not available, but whose positive and negative ions appear in the table. This table can also be used to obtain Λ_0 values for certain weak electrolytes such as acetic acid and carbonic acid. The limiting conductances for such electrolytes can not be determined by direct measurements of conductance, since the extrapolation from such data is inaccurate or impossible.

Another use of the constants given in Table II is to obtain limiting transference numbers used, for instance, in equations (19) and (20), the value for the negative ion constituent, t_0^-, being given by the relation

$$t_0^- = \frac{\lambda_0^-}{\lambda_0^+ + \lambda_0^-}. \qquad (33)$$

THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF WEAK ELECTROLYTES.

In the foregoing portion of this paper it has been shown that the interionic attraction theory, on which Onsager's equation is based, is of great utility in the interpretation of data on strong electrolytes. It has not been found necessary, in dealing with such electrolytes, to introduce the assumption that

they are incompletely dissociated. There is, however, a large group of electrolytes, of which acetic acid is typical, for which it is not possible to assume complete ionization of the aqueous solutions, and it is thus necessary to complicate the treatment by introducing a degree of dissociation. In dealing with data on such solutions the original Arrhenius theory was, as has been mentioned, moderately successful. It will be shown, however, that this apparent agreement with the early theory is due, from our present point of view, to a partial compensation of two errors.

Aqueous solutions of salts are nearly all strong electrolytes. In a solution of a weak acid which may be represented by HA, A representing the negative radical, the equilibrium

$$HA = H^+ + A^-$$

exists between the ions and the undissociated acid. For such an equilibrium the thermodynamic ionization constant is given by the relation

$$\frac{C\alpha^2}{(1-\alpha)} \cdot \frac{f_H f_A}{f_{HA}} = \mathbf{K}, \tag{34}$$

in which f_H, f_A, and f_{HA} are the activity coefficients of the hydrogen ion, the negative ion, and the undissociated acid respectively. Equation (34) is equivalent to the Ostwald dilution law, equation (2), without the assumption that the constituents are all normal solutes. However, as we have seen, Arrhenius and, following him, Ostwald computed α from the ratio Λ/Λ_0, a procedure which makes no allowance for the change of ion mobilities with the changing ion concentration. As has been shown in this paper, such changes are to be expected even in very low concentrations. A more nearly correct value of the degree of dissociation, α, may be obtained by the use of the expression

$$\frac{\Lambda}{\Lambda_e} = \alpha, \tag{35}$$

in which Λ is the equivalent conductance at the concentration C and Λ_e is the equivalent conductance of the electrolyte in a completely dissociated condition, and at the ion concentration $C\alpha$.

The following method for computing Λ_e will make this conception clear. As an example the value of Λ_e for acetic acid as a function of the ion concentration will be obtained. The computation depends upon two assumptions for which evidence has been given in this paper: (*a*) aqueous solutions of sodium chloride, sodium acetate, and hydrochloric acid are completely dissociated, and (*b*) at low ion concentrations the equivalent conductance, λ, of the ion constituents of strong electrolytes are independent of the nature of the associated ions, i.e., they follow Kohlrausch's law of independent ion migration. Thus if completely dissociated acetic acid were capable of existence the value of its equivalent conductance $\Lambda_{e\ HAc}$ would be in accord with the relation [10, 11, 12]

$$\Lambda_{e_{HAc}} = \Lambda_{HCl} + \Lambda_{NaAc} - \Lambda_{NaCl} \qquad (36)$$

since, in terms of ion conductance, λ, values

$$\Lambda_{e_{HAc}} = \lambda_H + \lambda_{Ac} = \lambda_H + \lambda_{Cl} + \lambda_{Na} + \lambda_{Ac} - \lambda_{Na} - \lambda_{Cl} \qquad (37)$$

all the terms except λ_H and λ_{Ac} cancelling. The equivalent conductances, Λ, in equation (36) are all known as functions of the concentration, C, so that values of Λ_e for completely dissociated acetic acid may be obtained as a function of the ion concentration, $C\alpha$. With the aid of conductance data on sodium chloride, hydrochloric acid, and sodium acetate, and recalling that the concentration C of a strong electrolyte must be replaced by ion concentration, $C\alpha$, for a weak electrolyte the equivalent conductance of completely dissociated acetic acid, $\Lambda_{e_{HAc}}$, may be shown to be given by the equation

$$\Lambda_{e_{HAc}} = 390.71 - 148.57\sqrt{C\alpha} + 163.2\, C\alpha(1 - 0.2273\sqrt{C\alpha}). \qquad (38)$$

The computation of the degree of dissociation with the aid of equations (35) and (38) requires a short series of approximations, since the value of Λ_e chosen must be that corresponding to the ion concentration $C\alpha$. A first approximation may be made using $\Lambda_e = \Lambda_0$ in equation (35), and with this preliminary

[10] C. W. Davies, *J. Phys. Chem.*, **29**, 977 (1925).
[11] M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).
[12] D. A. MacInnes, *ibid.*, **48**, 2068 (1926).

value of α an estimate of Λ_e from equation (38) may be obtained which in turn may be substituted in equation (35). This procedure may be continued until repetition fails to change the result. With the conductance data on acetic acid of Shedlovsky and MacInnes [13] and computations of the values of degrees of dissociation, α, computed as has just been described, values of the "dissociation function," $\mathbf{K}'$, defined by the relation

$$\mathbf{K}' = \frac{\alpha^2 C}{(1 - \alpha)} \tag{39}$$

may be obtained. These $\mathbf{K}'$ values are not constant, as would be the case if Ostwald's dilution law were valid, but increase with increasing concentration. The dissociation function $\mathbf{K}'$ is, from equation (34), connected with the thermodynamic ionization $\mathbf{K}$ by

$$\mathbf{K}' \frac{f_H f_A}{f_{HA}} = \mathbf{K}. \tag{40}$$

Since undissociated acetic acid is a non-electrolyte its activity coefficient, f_{HA}, may, with little error, be assumed to be unity. At very low concentrations the ion activity coefficients f_H and f_A may be expected to follow the limiting Debye-Hückel relation, which at 25° is

$$-\log f_H = -\log f_A = 0.5065 \sqrt{C\alpha}, \tag{41}$$

in which the product $C\alpha$ is the ion concentration. With this relation equation (40) may be put into the form

$$\log \mathbf{K} = \log \mathbf{K}' - 1.013 \sqrt{C\alpha}. \tag{42}$$

Thus if our reasoning is correct a plot of the logarithm of the dissociation function $\mathbf{K}'$ against $\sqrt{C\alpha}$ should be a straight line with a slope of 1.013 and an intercept equal to the logarithm of the thermodynamic dissociation constant $\mathbf{K}$. Such a plot is shown in Fig. 9. The straight line, *e*, has a slope equal to 1.013 as required by equation (42) and passes accurately through the six points corresponding to the measurements at the lower concentrations. The range of ion concentration

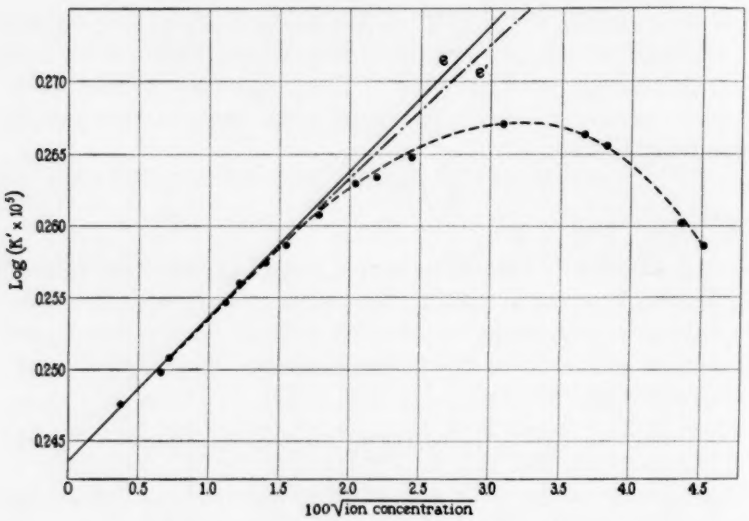
[13] MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

involving these six points is 0.000015 to 0.00015 mole per liter. These results and others of the same nature afford an accurate test of the *limiting* Debye-Hückel relation

$$-\log f = A\sqrt{C\alpha}.$$

However, at somewhat higher concentrations there is a rapid divergence from the requirements of the simple theory, as is shown by the decided bending away of the curve through the

FIG. 9.



experimental points from the straight line *e*. The use of the Debye-Hückel expression

$$-\log f = \frac{A\sqrt{C\alpha}}{1 - \beta a_i\sqrt{C\alpha}} \qquad (43)$$

produces agreement to but slightly higher ion concentrations, as is shown by the curve *e'*, which corresponds to the reasonable value of the "distance of closest approach," a_i, of 4Å for the hydrogen and acetate ions.

It must, however, be recalled that as the concentration of acetic acid is increased the solvent progressively changes from

pure water to a mixture of water and undissociated acetic acid. The properties of undissociated acetic acid are quite different from those of water. The acid has, for instance, a dielectric constant less than ten per cent. that of water, and its presence in aqueous solutions would be expected to influence the mobilities and the activities of the ions.

As already stated the limiting value of $\mathbf{K}'$ is the thermodynamic ionization constant, $\mathbf{K}$, which in this case is 1.753×10^{-5}. Another method for obtaining thermodynamic ionization constants depends on measurements of the electromotive force of concentration cells without liquid junctions. Using that method, Harned and Ehlers found 1.754×10^{-5} for the ionization constant of acetic acid at 25°. However, that constant is based on molalities, m, rather than concentrations, C. The relation between the ionization constants may be readily shown to be

$$\rho_0 \mathbf{K}_m = \mathbf{K}_C, \tag{44}$$

in which ρ_0 is the density of the solvent, in this case water. The correction lowers the value of the constant based on the e.m.f. measurements to 1.749×10^{-5}. However, the two results are in substantial agreement, although the determinations are based on quite different principles and experimental procedures.

SUMMARY.

Since the Debye-Hückel theory clearly indicates, from thermodynamic considerations, that strong electrolytes are substantially completely dissociated in aqueous solutions, it has been necessary to replace, in the explanation of the conductances of such electrolytes, the Arrhenius theory, which assumes partial dissociation and constant ion mobilities, with a theory which provides for changing mobilities with increasing ion concentrations. To this end Debye and Hückel, and Onsager, suggest two mechanisms: the "electrophoretic effect" and "the time of relaxation effect," both dependent upon interionic electrostatic attractions and repulsions. Experimental tests of Onsager's relations show that his equations account accurately, at least for very dilute solutions, for the changes with concentration of the conductances of solutions of electrolytes containing ions of widely differing mobilities and

valencies. For higher concentrations semi-empirical equations are available. In contrast to the Arrhenius theory, the newer ideas call for changes in the transference numbers with the concentration, which have been found experimentally. Precision transference measurements have also furnished an experimental test of Kohlrausch's law of independent mobilities of ions. The theory of interionic attractions and repulsions is, in addition, of utility in dealing with the ionic part of solutions of weak electrolytes. By computing degrees of dissociation in a manner which allows for changing ion mobilities a test is obtained of the Debye-Hückel limiting relation connecting activity coefficients with ion concentrations.

SOLUTIONS OF ELECTROLYTES IN NON-AQUEOUS SOLVENTS.

BY

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I. INTRODUCTION.

The power to dissolve electrolytes and to form electrolytic solutions is a property which, with few exceptions, is common to all liquids. A comprehensive review of this extensive field cannot be given on this occasion. At best, it will be possible to sketch only briefly such theoretical relationships as have been developed, to indicate their limitations and to suggest lines of investigation that seem to be promising.

Water, aside from its power of dissolving a great variety of inorganic electrolytes, is in no wise an exceptional solvent. Because of its high dielectric constant, dilute solutions of electrolytes in water exhibit simpler properties than do corresponding solutions in solvents of lower dielectric constant. While water dissolves inorganic electrolytes, and, particularly, electrolytes of higher type, to an extraordinary degree, the variety of electrolytes which it is capable of dissolving is more limited than is that of certain non-aqueous solvents. Salts of weak acids are largely, if not completely, hydrolyzed in water, while many salts, possessing ions, having a reducing power greater than that of hydrogen, are unstable in water.

In contrast to water, salts of weak acids in liquid ammonia are stable. Thus, it is possible to obtain solutions of such electrolytes as $KC(C_6H_5)_3$, $NaGeH_3$, $NaAsH_2$, Na_4Pb_9, Na_4Sn_8 and many others. So also we have solutions of the alkali metals and the metals of the alkaline earths in liquid ammonia, in which the negative electrons, due to these metals, function as anions. It is evident that much is to be gained from a study of solvent media, other than water, wherein solutions of electrolytes may be obtained which are not capable of existing in water.

The problem of electrolytic solutions is essentially that of the Coulombic interaction between ions. In the general case, both short and long range interactions must be taken into account, but in solvents of high dielectric constant, the short range interactions play no significant role at lower concentration.

When the dielectric constant of the solvent medium is low, it is not only necessary to take into account the short range interaction between ions and ions but also the interaction between ions and ion dipoles (ion pairs) as well as the interaction between dipoles and dipoles and, in many instances, interactions of still higher order.

II. LIMITING LAWS.

On the basis of the theory of ion interaction, certain limiting laws have been developed and established. These are the following:

$$-\log_{10} f = \beta\sqrt{\gamma C}, \tag{1}$$

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{\gamma C}), \tag{2}$$

$$\frac{c\gamma^2}{1-\gamma} f^2 = K, \tag{3}$$

$$\frac{1}{K} = \frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)^3 Q(b).* \tag{4}$$

---

* $Q(b) = \int_2^b e^y y^{-4} dy$, where $y = \frac{e^2}{rDkT}$ and $b = \frac{e^2}{aDkT}$. Here, r is the distance from a central charge, a is the distance between ions in contact (= sum of their radii), D is the dielectric constant of the solvent, T is the absolute temperature, k is Boltzmann's constant = 1.371 erg/1°, N is Avogadro's number = 6.06×10^{23} and e is the unit charge = 4.77×10^{-10} e.s.u. Other constants are:

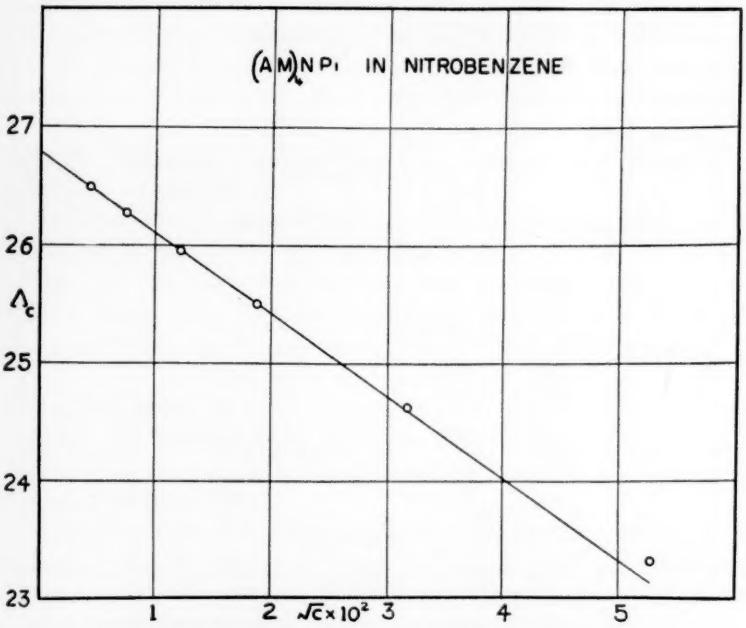
$$\beta = 0.4343\frac{e^2}{2DkT}\left(\frac{8\pi Ne^2}{1000DkT}\right)^{1/2}; \qquad \alpha = \frac{8.18 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{82}{\eta(DT)^{1/2}}$$

where η is the viscosity of the solvent, C is the equivalent concentration, Λ is the equivalent conductance, Λ_0 the limiting equivalent conductance, γ the degree of dissociation of the ion dipoles into free ions and $1/K$ the association constant of the ions (reciprocal of dissociation constant). f is the activity coefficient. The equations as written apply only to binary electrolytes. Nothing would be gained by using more general forms, since we have no data relating to solutions of salts of higher type in non-aqueous solvents at required concentrations.

Activity Coefficient.—Equation (1) has been well established as a limiting law for strong electrolytes in aqueous solution. In non-aqueous solutions, precise data are very limited, but such data as exist are in agreement with this relation.

Conductance in Solvents of High Dielectric Constant.—In water, a solvent of high dielectric constant ($D = 78$), where the value of γ is unity in accordance with equation (4), equation (2) is well established. For non-aqueous solutions of high dielectric constant, precise data are meagre, but such data as exist indicate that this relation is applicable. Recent measurements with solutions in nitrobenzene [1] ($D = 35$) bear this out (See Figure 1).

FIG. 1.



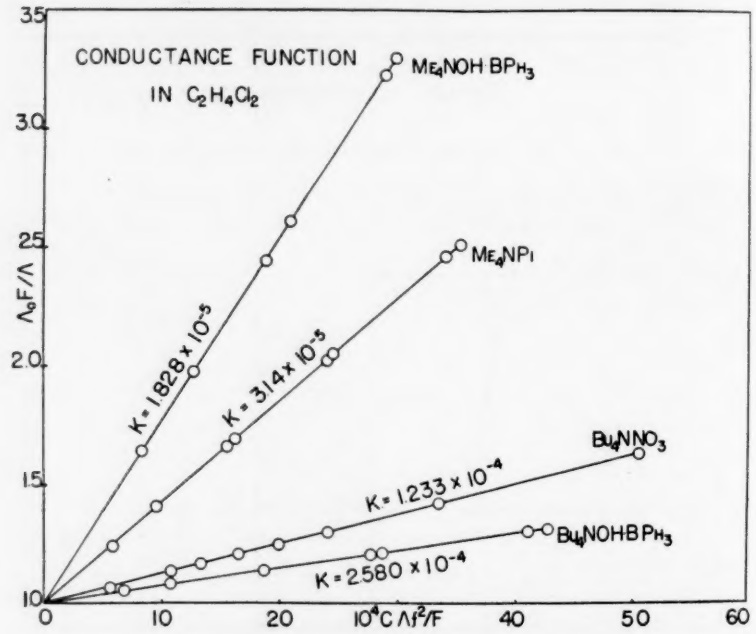
Onsager slope for completely dissociated electrolyte in nitrobenzene.

Lower Dielectric Constant.—In solvents of lower dielectric constant, where the value of γ is appreciably less than unity, it is necessary to combine equations (1), (2) and (3) in evaluat-

[1] Observations by Dr. E. G. Taylor in the Brown Laboratories.

ing conductance data. While an explicit solution of these equations is not available, convenient approximation methods have been developed by Dr. Fuoss [2] which make it possible to treat conductance data in such solvents with ease. All conductance measurements in solvents of lower dielectric constant, and many such measurements have been made with solutions of various electrolytes in ethylene chloride [3]

FIG. 2.



Plots for incompletely dissociated electrolytes in ethylene chloride.

(D = 10.3) and in pyridine [4] (D = 12.0), conform to the relationships required according to equation (1), (2) and (3). Examples are shown in Fig. 2, where the variables are so

[2] Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

[3] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935); Mead, Fuoss and Kraus, *ibid.*, **32**, 594 (1936); numerous unpublished observations made in the author's laboratory.

[4] W. F. Luder, Thesis, Brown University (1937); unpublished observations made in the author's laboratory.

chosen as to yield a linear relation so long as the equations hold.

Very Low Dielectric Constant.—In solvents of very low dielectric constant, where the fraction of electrolyte present as free ions is very small, equation (1) drops out and a combination of equations (2) and (3) takes the simple form:

$$\log_e \Lambda = -\tfrac{1}{2} \log_e C + K\Lambda_0^2. \qquad (5)$$

This relationship is followed by the conductance curves of all electrolytes where conductances have thus far been measured with some degree of precision at sufficiently low concentrations in solvents of very low dielectric constant. The linear form of the curves is shown in the lower part of Fig. 3 for solutions of tetra*iso*amylammonium nitrate in mixtures of dioxane and water.[5] Values of log Λ and log C are plotted as ordinates and abscissas, respectively.

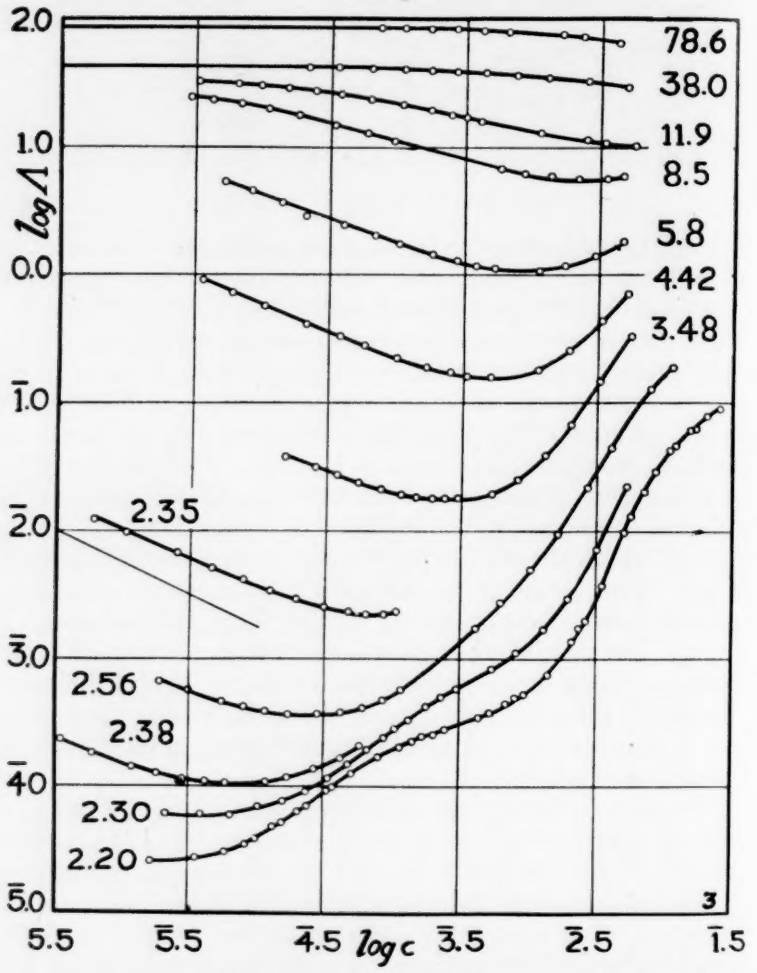
It is a general property of electrolytic solutions that, as the dielectric constant of the medium is diminished, a point is reached where the conductance curve passes through a minimum. With diminishing dielectric constant, the minimum shifts toward lower concentrations. This is illustrated in Fig. 3. For a mixture having a dielectric constant of 9, the minimum lies in the neighborhood of 0.01 N. As the dielectric constant of the mixture is diminished by increasing the proportion of dioxane, the minimum is shifted until, in pure dioxane, it lies at 3×10^{-5} N.

Ion-Dipole Interaction.—Since the minimum in dioxane or benzene solutions occurs at equivalent ion concentrations as low as 1×10^{-11} N, it follows that the increase in conductance at concentrations in the neighborhood of the minimum point must be due to something other than long range interaction between the ions; there must be some process occurring as a result of which the number of ions in solution is increased.

The force acting between an ion dipole and an ion varies inversely as the cube of the distance. In solvents of low dielectric constant, there is, therefore, a marked tendency for ions and ion pairs to interact at short distances to form triple ions according to the equations: $A^+ + AB = ABA^+$ (A) and $B^- + AB = BAB^-$ (B). In solvents of very low dielectric

[5] Kraus and Fuoss, *J. Am. Chem. Soc.*, **55**, 21 (1933).

FIG. 3.



Conductance curves for tetra*iso*amylammonium nitrate in dioxane-water mixtures, illustrating the influence of dielectric constant.

constant, the energy of the triple ions is sufficiently high (with respect to the energy of thermal agitation) to render them quite stable. Treating the interaction between ions and ion dipoles in the same manner as that between ions and ions,[6] we are led to equations for the association constants of reac-

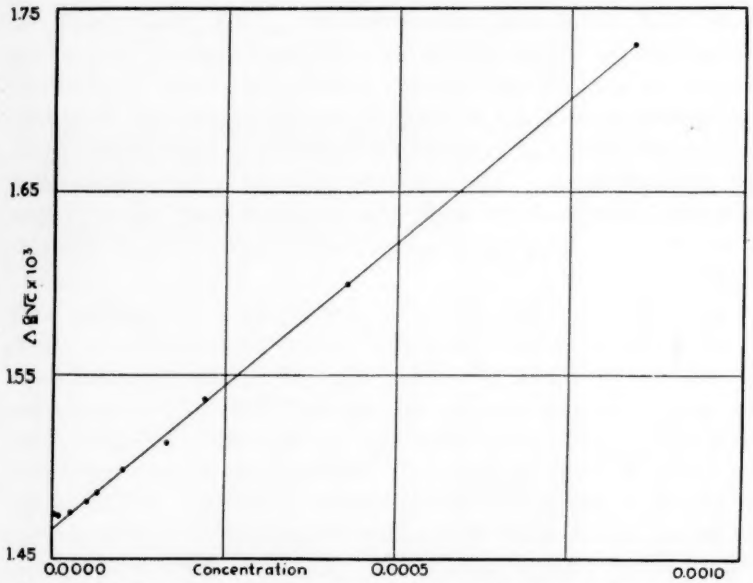
[6] Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

tions (A) and (B), which are similar to equation (4). The conductance equation in this case takes the form:

$$\Lambda\sqrt{C}\, g(C) = \Lambda_0\sqrt{K} + \frac{\lambda_0\sqrt{K}}{k} C, \qquad (6)$$

where $g(C)$ is a correction factor which takes into account the activity and molality terms. λ_0 is the equivalent conductance of the triple ions (assumed equal) and k is the dissociation constant, assumed equal for reactions (A) and (B). Accord-

FIG. 4.



Plot illustrating the triple ion effect in solutions of tetrabutylammonium picrate in anisole.

ing to this equation, the function $\Lambda\sqrt{C}\, g(C)$ varies linearly with the concentration. In the case of solutions in solvents of very low dielectric constant, the correction factor $g(C)$ becomes small or negligible and $\Lambda\sqrt{C}$ varies linearly with the concentration. Equation (6) has been shown to apply satisfactorily to solutions in solvents of lower dielectric constant as far as the minimum point.[7] An example is shown in Fig. 4.

[7] Ref. (6) and Cox, ref. (3).

At concentrations above the minimum, the conductance rises more rapidly than equation (6) indicates.

III. OTHER INTERACTIONS.

Structures of Higher Type.—Experimentally, it has been found that in solvents of very low dielectric constant, the conductance curves in the concentration region above the minimum point fall into two types, namely: those which are everywhere concave upward and those which exhibit several inflection points above the minimum [8] (Fig. 3). In the latter case, there is a region where the conductance increases very little with increasing concentration. This might well be interpreted as being due to interaction between dipoles and dipoles as a result of which quadripoles would be formed. The formation of these neutral molecules would tend to reduce the normal rate of increase in the number of ions with increasing concentration. This view is supported by independent evidence obtained through the measurement of dielectric constants and freezing points of solutions of electrolytes in benzene.

Ion Dipoles.—The dielectric constants of numerous solutions of electrolytes in benzene have been measured.[9] Here we are measuring properties of the ion dipoles rather than of the ions. The values for the limiting molecular polarization obtained for many electrolytes in benzene are very large, ranging from 1100 cc. to 8200 cc. Polarization curves are shown in Fig. 5. The polarization curves, generally, exhibit a decrease of value with increasing concentration, some curves being linear and others more complex. This decrease of polarization may be accounted for by assuming interaction between dipoles and dipoles with the formation of quadripoles. This problem of dipole interaction has been treated theoretically on the basis of an ellipsoidal, point, dipole model.[10] The degree of association depends, essentially, upon the value of

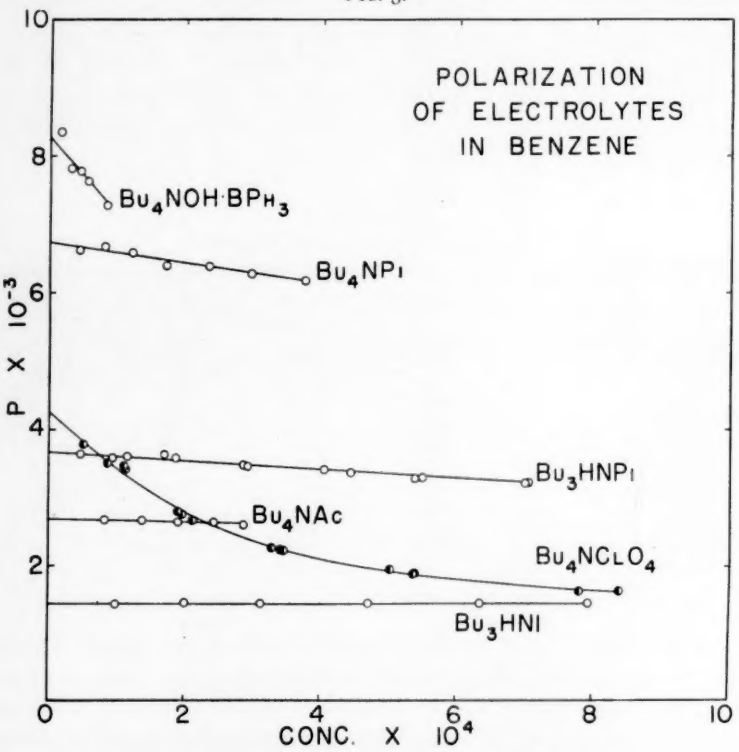
[8] Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 3614 (1933); Luder and P. B. Kraus, *ibid.*, **58**, 255 (1936).

[9] Hooper and Kraus, *J. Am. Chem. Soc.*, **56**, 2265 (1934); Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

[10] Fuoss, *J. Am. Chem. Soc.*, **56**, 1031 (1934).

the minor diameter and the value of the dipole moment.[11] Certain of the polarization curves show a rapid decrease in value with increasing concentration. The electrolytes here in question are the ones which exhibit a very flat portion in the conductance curve above the minimum. The inference is

FIG. 5.



Polarization curves of some electrolytes in benzene solution.

that, depending upon the dipole moment and the spatial configuration of the ions, association of dipoles is taking place with the formation of structures more complex than quadripoles.

Tributylammonium chloride, bromide and iodide show practically no change of polarization with concentration.[12]

[11] Fuoss, *J. Am. Chem. Soc.*, **56**, 1027 (1934); Fuoss and Kraus, *ibid.*, **57**, 1 (1935); Rothrock and Kraus, *ibid.*, **59**, 1699 (1937).

[12] Geddes, ref. (9).

Freezing point measurements show considerable association.[13] The inference is that these dipoles form two types of quadripoles, end to end and side by side (anti-parallel) in such proportions as to cause no change in polarization.

Using the polar moments derived from the limiting polarization, the polar moments of the ion dipoles may be computed. If these dipoles are, in fact, ion pairs, then the distance between centers of charge in the dipoles may be obtained by simply dividing the moment by the unit charge.* Values of P_0 (limiting polarization), μ (polar moment), a (distance between centers of charge) and λ_A (minor diameter of ellipsoidal dipole model) are given in Table I.

TABLE I.

Constants of Ion Dipoles in Benzene.

Salt.	P_0.	$\mu \times 10^{18}$.	$a \times 10^{8}$.	$\lambda_A \times 10^{8}$.
n-$Bu_4NOH \cdot BPh_3$	8270	19.7	4.13	6.37
i-Am_4NPi	7090	18.3	3.82	6.28
n-Bu_4NPi	6740	17.8	3.73	6.28
i-Am_4NSCN	5050	15.4	3.23	—
n-Bu_4NClO_4	4250	14.1	2.96	—
i-Am_3NHPi	3830	13.3	2.79	5.05
n-Bu_3NHPi	3670	13.1	2.74	5.02
n-Bu_4NBr	2900	11.6	2.43	—
n-Bu_4NAc	2690	11.2	2.35	4.59
n-Bu_3NHI	1440	8.09	1.69	—
n-Bu_3NHBr	1280	7.61	1.59	—
n-Bu_3NHCl	1140	7.17	1.50	—

The values of a in the fourth column are about thirty per cent. smaller than those computed from conductance measurements according to equation (4) for the same electrolytes in benzene solution. The discrepancy is not surprising when one recalls the imperfections of the model upon which equation (4) is based. Minor diameters of the ellipsoidal model, as computed from the slopes of the polarization curves, are given in the last column. These values seem reasonable in the light of what we know of atomic dimension as derived from other sources. Employing freezing point data for several

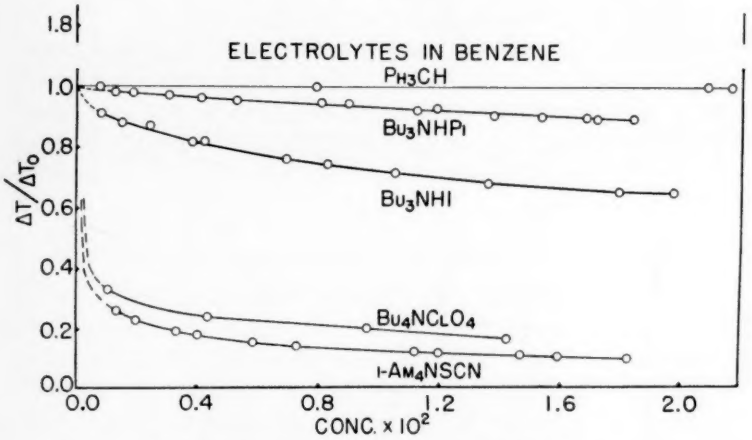
[13] Rothrock, ref. (11).

* In this computation, no account is taken of induced polarization due to the charges. Taking this factor into account should lead to larger values of a.

electrolytes in benzene, values obtained for the minor diameters have been found in good agreement with those obtained from polarization curves for the same electrolytes.[13a]

Molecular Weight.—The freezing point curves for electrolytes in benzene closely parallel the polarization curves.[14] Those electrolytes which exhibit a small linear decrease of polarization with concentration likewise show a small linear decrease in the value of $\Delta t/\Delta t_0$, where Δt is the observed freezing point lowering and Δt_0 is the ideal lowering at the same stoichiometric concentration. Freezing point curves are shown in Fig. 6. Those electrolytes which exhibit a sharp

FIG. 6.



Freezing point curves of some electrolytes in benzene.

decrease in the polarization likewise exhibit a sharp decrease in the value of $\Delta i/\Delta t_0$. The concentrations at which reliable freezing point measurements can be made in benzene (0.001 *N* and above) are much above those at which reliable dielectric constant measurements can still be made. In many cases, therefore, a high degree of association of dipoles is indicated at the lowest concentration at which the freezing point may be measured. With tetrabutylammonium thiocyanate, the

[13a] Reference 11.

[14] Kraus and Vingee, *J. Am. Chem. Soc.*, **56**, 511 (1934); Batson and Kraus, *ibid.*, **56**, 2017 (1934); Rothrock and Kraus, *ibid.*, **59**, 1699 (1937).

mean molecular weight, at 10^{-3} N, is approximately three times the formula weight and, at 0.02 N, it is eleven times the formula weight.

To account for the rapid rise in the conductance curves at higher concentrations, it is necessary to assume a rapid increase in the number of ions. If these ions are complex aggregates, containing a large number of simple ions, then their mobility can certainly not be higher than that of simple ions. The only process that suggests itself as accounting for the rapid conductance increase is that numerous equilibria exist among a variety of charged and uncharged aggregates of varying degrees of complexity.

Mixtures.—Very little work has been done with mixtures of electrolytes in solvents of low dielectric constant. The conductance of mixtures of tetrabutyl- and tetramethyl-ammonium picrates has been measured in ethylene chloride solution.[15] The results are in excellent agreement with the theory of mixtures as developed by Onsager and Fuoss.[16] No data are available with respect to mixtures in solvents of very low dielectric constant.

IV. INFLUENCE OF DIELECTRIC CONSTANT, SIZE AND STRUCTURE.

Dielectric Constant.—It remains to discuss equation (4). This equation is important in that it connects the association constant of the ions with the dielectric constant of the solvent and the size of the ions.[17] Let us first consider the dielectric constant. This constant enters in equations (1) and (2) as well as in (4), but in the former equations it influences the observed phenomena only in the long range Coulombic interactions and atomic dimensions do not enter. While the theoretical treatment of short range interactions involves the rather crude approximation that the macroscopic dielectric constant may be employed in short range interactions, nevertheless, lacking a more accurate approximation, the theory of short range interactions serves to account remarkably well for the observed results. The limitations of the theory, however,

[15] Mead, ref. (3).

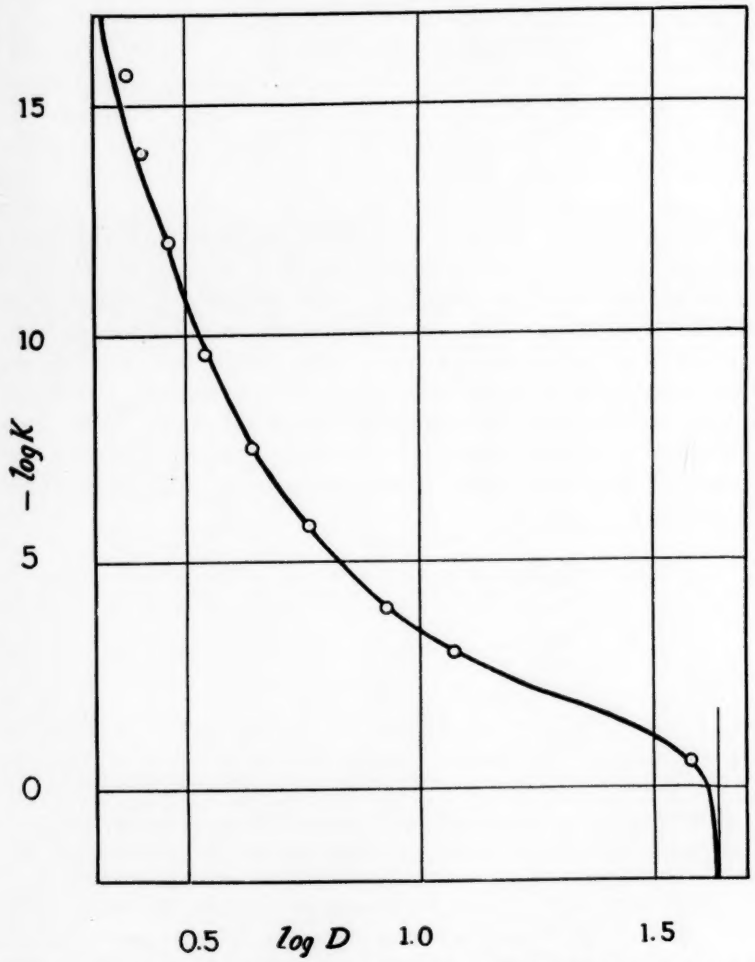
[16] Onsager and Fuoss, *J. Physic. Chem.*, **36**, 2689 (1932).

[17] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

should not be forgotten, particularly in relation to computed ion dimensions.

Equation (4) may be tested by means of the data obtained for solutions of tetra*iso*amylammonium nitrate in mixtures of dioxane and water (Fig. 3). Values of K for various dioxane-water mixtures have been computed from the conductance

FIG. 7.



Curve according to equation (4) based on $a = 6.4 \times 10^{-8}$ cm. Points for solutions of tetra*iso*-amylammonium nitrate in dioxane-water mixtures.

values. Computing the value of a for a given mixture, and assuming this value to be the same for the other mixtures, K has been computed as a function of D.[18] The curve is shown in Fig. 7, based on the value $a = 6.4 \times 10^{-8}$ cm. The curve has a very characteristic form and the dissociation constant, as measured, follows this curve within the limits of experimental error.

Effect of Ion Size.—We may now consider the relation between the properties of electrolytes and the constitution of their ions. If the dissociation constants of electrolytes are known, values of a may be computed according to equation (4). The values of a, so obtained, should lie in the neighborhood of 5×10^{-8} cm. and should be a function of the number of atoms in the ions, their size and spatial arrangement. In any case, however imperfect the model, values of K should vary in a regular manner with the complexity of the ionic structures. Many electrolytes have been studied in ethylene chloride and pyridine solution. The computed values of a usually range between 4 and 7 Ångström units, although both smaller and larger values have been found for electrolytes with very small or very large ions. The values show definite relation to the size and configuration of the ions. With ions of similar type, but containing a varying number of atoms, the value of a increases regularly with increasing number of atoms as shown in Table II.

TABLE II.

Constants of Quaternary Ammonium Picrates in Ethylene Chloride.

Salt.	Λ_0.	$K \times 10^4$.	$a \times 10^8$.
*Me_4NPi [15]	73.81	0.326	4.19
Et_4NPi [19]	69.52	1.59	5.30
n-Pr_4NPi [19]	61.82	1.95	5.54
n-Bu_4NPi [15]	57.40	2.28	5.75
n-Am_4NPi [19]	54.50	2.39	5.81
i-Am_4NPi [19]	55.11	2.39	5.81

* Me = methyl, Et = ethyl, Pr = propyl, Am = amyl, Pi = picrate, Bu = butyl.

Structure.—In dealing with ions of complicated structure, such as the substituted onium ions of nitrogen, phosphorus,

[18] Fuoss and Kraus, ref. (17).

[19] L. M. Tucker, unpublished observations in the author's laboratory.

sulfur and iodine, it is not only the size of the substituent groups that determines the dissociation constant of the electrolyte, their spatial arrangement must also be taken into account. In ethylene chloride, for example, triphenylethylphosphonium picrate [20] ($K = 3.76 \times 10^{-4}$) is stronger than triphenylethylphosphonium perchlorate ($K = 3.60 \times 10^{-4}$). In the case of the diphenyliodonium ion,[21] however, the picrate ($K = 0.0233 \times 10^{-4}$) is decidedly weaker than the perchlorate ($K = 0.115 \times 10^{-4}$). It seems reasonable to ascribe this inversion to the dumb-bell shape of the iodonium ion and to the localization of charge on the oxygen atom of the picrate ion and stearic effects, due to the adjacent nitro groups. There are many other examples of the influence of structure on the dissociation constant of electrolytes.

Influence of Substituent Atoms.—Not only do structure and configuration have an influence on the strength of an electrolyte, the nature of the atoms that appear in the ions also has a marked effect. The dissociation constants of a number of choline picrates are given in Table III.[22] As may be seen from

TABLE III.

Constants for Choline Picrate in Ethylene Chloride.

Salt.	Λ_0.	$K \times 10^4$.
$Me_3 \cdot Et \cdot NPi$	73.30	0.460
$Me_3 \cdot CH_3OCH_2 \cdot NPi$	71.40	.254
$Me_3 \cdot CH_3COOC_2H_4 \cdot NPi$	66.10	.196
$Me_3 \cdot BrC_2H_4 \cdot NPi$	68.50	.132
$Me_3 \cdot ClC_2H_4 \cdot NPi$	69.00	.125
$Me_3 \cdot ICH_2 \cdot NPi$	67.00	.110
$Me_3 \cdot BrCH_2 \cdot NPi$	69.90	.078
$Me_3 \cdot HOC_2H_4 \cdot NPi$	71.60	.066
$Me_3 \cdot HOCH_2 \cdot NPi$	59.67	.093

the table, the constant of ethyltrimethylammonium picrate (0.460×10^{-4}) is nearly seven times that of hydroxyethyltrimethylammonium picrate ($K = 0.066 \times 10^{-4}$). Other interesting relationships will be evident upon inspection of the table; the exceptionally low conductance of hydroxymethyltrimethalammonium picrate indicates interaction of the positive ion with the solvent, due to the hydroxyl group.

[20] L. F. Gleysteen, unpublished observations in the author's laboratory.

[21] E. R. Kline, unpublished observations in the author's laboratory.

[22] Observations by D. J. Mead, D. A. Rothrock and J. B. Ramsey.

As yet, it cannot be said whether these effects are due to the dipole moments introduced into the ions or to other factors. It is apparent that the nature of the atoms, particularly electronegative atoms, in the positive ion, has a decided influence on the strength of the electrolyte. Whether this is also true of the negative ion has not as yet been established. Scattered data indicate that the introduction of negative atoms into the negative ions does not diminish the dissociation constant. If such substitution increases the constant, the increase cannot be large.

V. WEAK ELECTROLYTES AND SOLVENT INTERACTION.

Weak Salts.—The preceding discussion has related, in the main, to what may be termed normal electrolytes, that is, compounds which, in the solid state, possess an ionic lattice. Nearly all salts of strongly positive ions, regardless of the negative ion, belong to this type. Salts of strongly electronegative ions and weakly electropositive ions are, in general, weak electrolytes in all solvents and it is probable that, in many cases, quantum forces, as well as Coulombic forces, must be taken into account in considering the interaction be-between their ions. In many cases, too, interaction with the solvent is important. The nature of electrolytic solutions of very low conductance is not well understood; they deserve further study.

Acids and Bases.—There are many substances which interact with molecules of the solvent, particularly solvents of the ammonia or the water type, to form relatively strong electrolytes. Typical examples are acids and bases in water. In the case of the acids, proton intercharge between the solute and the solvent molecules is involved and the same is true of the nitrogen and other similar bases. In solvents which have no proton affinity, the acids are extremely weak electrolytes. They seem to exhibit some conducting power, but accurate data are lacking. In some instances, certain acids, such as perchloric acid, exhibit a fairly high conductance in solvents such as nitrobenzene. It is to be expected that the behavior of acids in *a*-protic solvents will be largely dependent upon the firmness of bonding of the proton by the negative constituent of the solute.

Protonic Interactions.—The primary, secondary and tertiary amines are weak bases in water, having dissociation constants of the same order as that of ammonia, although, usually, somewhat stronger. The completely alkylated or arylated onium bases are all strong electrolytes. Salts derived from the amines are strong electrolytes in water. In solvents of lower dielectric constant, where the quaternary salts are markedly dissociated, the amine salts are either normally dissociated or very slightly dissociated, depending upon the nature of the solvent. Thus, in nitrobenzene, monobutylammonium picrate has a dissociation constant of 1.5×10^{-4}, while tetrabutylammonium picrate conforms to the Onsager slope, indicating complete dissociation. In ethylene chloride, where the dissociation constant of tetrabutylammonium picrate is 1.6×10^{-4}, the dissociation constant of tributylammonium picrate is of the order of 1.5×10^{-8}.

When dissolved in a solvent that has a marked affinity for the proton, the amine salts have normal strength. This is indicated by the normal value of the dissociation constants of ammonium salts in liquid ammonia and in pyridine. Pyridonium nitrate in pyridine has a dissociation constant of 0.5×10^{-4}, while in ethylene chloride, the dissociation constant of the picrate is of the order of 1×10^{-8}. The difference in behavior of these salts in different types of solvents is doubtless due to the presence of the proton in the positive ion. In solvents that have no affinity for the proton, there is a specific interaction, due to the proton, between the positive and the negative ion. In a solvent such as pyridine, which has a marked affinity for the proton, interaction takes place between the proton and the solvent molecules, rather than between the proton and the negative ion. Further investigation is required to fully elucidate the interaction that occurs in systems of this kind.

Other Interactions.—The conductance of many other substances depends upon interaction between the solute and the solvent molecules. Triphenylmethylchloride, for example, is a good electrolyte in ammonia or in sulfur dioxide but a very poor electrolyte in nitrobenzene. Similarly, trimethyltin chloride is a good electrolyte in alcohol, although it is distinctly weaker than normal salts ($K = 0.35 \times 10^{-4}$), while

it is a very weak electrolyte in nitrobenzene and other similar solvents.[23] The electrolytic properties of solutions of substances of this kind are due to interaction of the positive constituent of the solute molecule with the solvent molecules. Thus, when trimethyltin chloride is dissolved in ammonia, a molecule of ammonia combines with the trimethyltin group to saturate the fourth valence of tin by coordinated linkage, the group, as a whole, being positive. In the resulting compound, the chlorine is linked to this group only through Coulomb forces. Where the solvent molecule cannot form such coordinated linkages with the positive constituent, the compound is a weak electrolyte.

The strength of electrolytes of this type also depends upon the nature of the negative constituent. Thus, while triphenylmethyl chloride is a poor electrolyte in nitrobenzene, triphenylmethylperchlorate is a rather good electrolyte. The greater dissociation of the perchlorate with respect to that of the chloride is doubtless due to the weaker bonding of the perchlorate and the triphenylmethyl groups. Similar relations hold with other groups such as triphenyltin, alkyl and aryl mercury, and the like.

Compounds with large positive ions and small negative ions are usually much weaker electrolytes than corresponding compounds of larger negative ions. Thus, of the halide salts of the tetrabutylammonium group, the iodide is the strongest and the fluoride is the weakest electrolyte in benzene solution.[24] If small anions are combined with large neutral groups, the resulting compounds become strong electrolytes. Thus, the fluoride ion readily adds triphenylboron and the resulting compound, tetrabutylammonium fluorotriphenylboron, is a very strong electrolyte in all solvents ($K = 2.07 \times 10^{-4}$ in ethylene chloride). So, also, sodium amide in liquid ammonia is an exceedingly weak electrolyte, while sodium ammidotriphenylboron is a very strong electrolyte.

Solvation.—The interaction between normal ions and solvent molecules remains very obscure. There is, however, ample evidence indicating that in solvents having polar mole-

[23] Kraus and Callis, *J. Am. Chem. Soc.*, **45**, 2624 (1923).

[24] Fuoss and Kraus, ref. (8).

cules, there is considerable interaction between the ions and the solvent, in some cases, perhaps, with the formation of definite solvates. This is indicated, for example, by the limiting conductance values of various ions. In ethylene chloride, the acetate ion has a conductance of 26.60, while the picrate ion, which is much larger, has a conductance of 31.20. The exceptionally low value of the conductance of the acetate ion in ethylene chloride can only be accounted for by interaction between the carboxyl group and the ethylene chloride molecules. It is of interest to note that the acetate ion has an exceptionally low conductance in water. That the solvent molecules, in the case of the acetate ion in ethylene chloride, are not held very firmly is indicated by the fact that the dissociation constant of tetrabutylammonium acetate is 1.36×10^{-4}, while that of the corresponding picrate is 2.28×10^{-4}.

VI. SOME OTHER PROPERTIES OF ELECTROLYTIC SOLUTIONS.

Temperature Effects.—The influence of temperature on conductance in non-aqueous media has not been extensively investigated. Temperature has a manifold influence on the properties of an electrolytic solution. It appears as a parameter in equations (1), (2) and (4) and, thus, has an influence on ion interaction, both long and short range; it has a marked influence on the viscosity of the medium and, finally, upon the dielectric constant of the solvent. Solutions of several electrolytes in anisole have been measured [25] over the temperature range from $-33°$ to $95°$. The results are in reasonably good agreement with equations (1), (2) and (3). There is need for further work in this field.

Viscosity Effects.—The relation between conductance and viscosity is very incompletely understood. Roughly, the conductance is proportional to the fluidity of the solution or, in the case of dilute solution, to the fluidity of the solvent medium. The relation, however, is not an exact one and the deviations from Walden's rule are often large. In many non-aqueous solvents, the product $\Lambda_0\eta$ (η = viscosity) has a value of approximately 0.5, but for water, ammonia and sulfur dioxide, the product is much larger, while for the higher alco-

[25] Bien, Fuoss and Kraus, *J. Am. Chem. Soc.*, **56**, 1860 (1934); see, also, Fuoss, *ibid.*, p. 1837.

hols, it is much smaller. The constancy of the product $\Lambda_0\eta$ depends upon the nature of the ions. The greater the mobility of the ions, the greater are the deviations from constancy. Doubtless, interaction between the ions and the solvent molecules is involved. It might be expected that such interaction would be greater in the case of small ions than in that of large ions, and that the detailed structure of the solvent molecule would have a marked influence on the nature of the interaction. That the product $\Lambda_0\eta$ should vary greatly in different solvents is in no way surprising.

Potential and Frequency Effects.—The Wien potential effect for strong and weak electrolytes and the Debye-Falkenhagen frequency effect have been well established in the case of aqueous solutions and have been found to be in excellent agreement with the ion atmosphere theory. These effects have not as yet been studied very extensively in non-aqueous solutions, particularly of lower dielectric constant. A systematic investigation of this field should yield valuable results.

VII. CONCLUSION.

Much remains to be done in the field of electrolytes in non-aqueous solution. A greater number of solvent and solute types needs to be investigated, including solvents having dielectric constants higher than that of water, as well as lower. The influence of temperature requires investigation over the widest possible range. Electrolytes, other than those commonly employed, need to be studied over a wide range of conditions, particularly such electrolytes as yield solutions of low conducting power. The study of solvents should be extended to include solvents of high viscosity, including plastic media. Two-phase systems and surface phenomena require attention. Our knowledge of colloidal electrolytes in non-aqueous solution is very deficient. The interaction of ions with solvent molecules and the precise nature of the ions themselves remain to be determined. Mixtures of electrolytes require investigation.

On the theoretical side, the outstanding problem is that of concentrated solutions. Many experimental data are available, but they remain uncorrelated. There is, as yet, no theory of concentrated solutions of electrolytes. In solvents

of low dielectric constant, there is reason to believe that in physically dilute systems ($C = 10^{-2}$ to 10^{-5} N), a multiplicity of equilibria exists between neutral and charged molecules of many different degrees of complexity. In more concentrated systems, phenomena may intervene of an entirely different type. In the light of our present knowledge, it seems safe to predict that the solution of the problem of electrolytes will probably not be found through a mere extension of the limiting laws that hold only at very low concentrations.

In the field of electrolytes, as in most other fields of science, painstaking and accurate experimental work must precede further theoretical advance. Such experimental work needs to be carefully planned and the systems studied need to be carefully selected. The problem of electrolytes is a broad one, the number of solvent types, like the number of electrolyte types, is very large. Water has served a useful purpose in the development of the field of electrolytes, but it is only one of many solvents and the properties of aqueous solutions are limited by the physical and chemical properties of the solvent itself.

February, 1938.

"Packaged" Boiler.—(*Power*, Vol. 82, No. 4.) When Nicholson File Co. decided that more steaming capacity was needed for their Philadelphia plant, a thorough study of the field was made to select a modern, efficient unit which could set a pattern for possible future boiler plant modernization. The boiler installed is another example of a trend in the power field, the idea of a "packaged" unit. In this case, boiler, oil burner, and auxiliaries were bought and delivered as a unit, mounted on a structural steel base, ready to operate as soon as proper piping and electrical connections were made. Essentially a fire tube boiler of the Marine type, redesigned for efficient oil burning operation, the new "Oilbilt" boiler is rated at 17,000 lb. per hour and is built for 150 lb. steam pressure. An efficiency of 80 per cent. is guaranteed by the Cleaver-Brooks Co. of Milwaukee, the manufacturers. Contributing to this high efficiency is the 4 pass down draft arrangement of passages giving long draft travel. A horizontal rotary oil burner is equipped with special controls and a blower for primary and secondary air, designed to proportion air and oil in the correct ratios for all loads from 20 per cent. to full rating, resulting in a CO_2 range of 13.5 to 14 per cent. The burner controls regulate its operation on the high-low flame cycle, in accordance with boiler pressure, and a complete set of protective devices takes care of motor overload, flame failure, or low water. Since all draft requirements are met by the blower, which is V-belted to an induction motor below the operating platform, no stack is necessary. In this case, the vent pipe, rises about 8 ft. above the roof of the boiler house, a one story building. Among the advantages claimed to accrue from the fact of the unit design are simplification of preliminary engineering studies, a block of steam generating capacity of guaranteed efficiency is bought, installation is comparatively easy and possible future boiler house changes are facilitated. It is also claimed that factory assembly permits preliminary operation and adjustment of controls, and making evaporation tests before delivery.

R. H. O.

KINETICS IN IONIC SYSTEMS.

BY

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For many years the rates of reaction between ionic species constituted one of the enigmas of physical chemistry. The rates varied with the concentration of the reactants, the presence of neutral salts, and with the progress of the reaction in a fashion which was so puzzling that prominent investigators (for example, Nernst) held the view that they could not be reconciled with the well-established laws of chemical kinetics valid for uncharged molecules.

The preceding speakers (MacInnes, Harned and Kraus) have reviewed to date the evidence which establishes that the peculiarities of conductance, and the thermodynamic properties of e.m.f., solubility, freezing point depression, etc., can be adequately interpreted on the Coulombic laws of electrostatics particularly with the aid of the original Debye-Hückel and later modifications of that theory.

It remains only to demonstrate that the kinetic behavior of ionic systems is likewise amenable to an analogous electrostatic treatment. These investigations have recently turned up a number of new and interesting problems peculiar to the general problem of reaction kinetics, which show that reaction velocity is still in its swaddling clothes as compared to the thermodynamic and conductive properties.

The fundamental kinetic concepts as applied to ionic systems are due almost exclusively to Brönsted, but the subsequent appearance of the Debye-Hückel theory and the rapid development of the theory underlying chemical kinetics have enabled a number of workers to make significant contributions, extending, limiting and clarifying Brönsted's penetrating ideas.[1-9]

[1] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925); *Trans. Far. Soc.*, 1928.

[2] Bjerrum, *ibid.*, **108**, 82 (1924); **118**, 251 (1925).

Consider two uncharged molecules A^0 and B^0 of molecular weight M_A and M_B, with radii r_A and r_B, which react bimolecularly to form the resultants $R_1 + R_2 + \cdots$. The molar rate of reaction k should be proportional to the number of collisions, Z between A and B; i.e. to Z^0, the collision frequency, when $C_A = C_B =$ Unity.

$$Z^0 = \frac{Z}{N_A N_B} = (r_A + r_B)^2 \sqrt{8\pi RT\left(\frac{1}{M_A} + \frac{1}{M_B}\right)}$$

per cc. per sec. (1)

Since only a small fraction of the total collisions prove fruitful, the familiar concept of activated or critical complexes suggested by Arrhenius and clarified by Marcelin must be introduced. Only those collisions which produce a critical transition state complex X possessing the activation energy E will react. Collision complexes of lower energy content are deactivated by collisions with the solvent and return to the normal state $A + B$.

Hence

$$k = Z^0 e^{-E/RT}. \qquad (2)$$

Eq. (2) holds remarkably well for gaseous reactions and in a sufficiently large number of solution reactions to warrant its use as a pictorial approximation. E is defined as[10, 11]

$$RT^2 \frac{d \ln k}{dT}. \qquad (3)$$

This treatment, while open to serious objections of oversimplification, will serve satisfactorily for the moment in

[3] Christiansen, *ibid.*, **113**, 35 (1924).

[4] Scatchard, *J. Am. Chem. Soc.*, **52**, 52 (1930); *Chem. Rev.*, **10**, 229 (1932).

[5] La Mer, *J. Am. Chem. Soc.*, **51**, 3341 (1929); **53**, 2832 (1931); **54**, 2351, 2739 (1932); **55**, 1739 (1933); **57**, 2662 (1935); *Chem. Rev.*, **10**, 179 (1932); *J. Chem. Phys.*, **1**, 289 (1933).

[6] Warner, *ibid.*, **55**, 4807 (1933); **57**, 1491, 1883 (1935).

[7] Skrabal, *Trans. Far. Soc.*, **24**, 687 (1928).

[8] Svirbely, *J. Am. Chem. Soc.*, **60**, 330 (1938). (With Schramm.)

[9] Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

[10] Tolman, Statistical Mechanics, Chem. Catalog Co., pp. 259–69 (1927).

[11] La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

elucidating the principal effects of electric net charges upon the rate of reaction.

When only two molecules A and B are present in the volume V, it is obvious that the addition of electric charges to produce ions will depress or increase the rate at which $A + B$ would normally react, depending upon the sign of the net charges z_A and z_B. If the product $z_A z_B$ is negative corresponding to $A^+ + B^- \rightleftharpoons X^0$ or $A^- + B^+ \rightleftharpoons X^0$, the rate will be increased since ions of opposite sign will collide more frequently; conversely for ions of the same sign; if $z_A z_B$ is positive, the rate will be decreased. The collision of two ions of the same sign can only occur when energy of thermal agitation along the line of approach, $RT/2N$, is sufficient to overcome the mutual electrostatic energy of repulsion

$$\frac{z_A z_B \epsilon^2}{2D} \cdot \frac{1}{(r_A + r_B)}.$$

Here D is the dielectric constant, $r_A + r_B$ the distance of closest approach of the centers of A and B necessary for chemical reaction.

The variation in collision number and therefore the increase in rate of reaction, $\Delta \log k$, as will be shown more rigorously later, is given in this simple case of two ions by a term

$$\Delta \log k = - z_A z_B \frac{\epsilon^2 N}{DRT} \cdot \frac{1}{(r_A + r_B)}.$$

ϵ is the unit electrostatic charge and R and N have their usual significance.

Unfortunately the rate of reaction between single ions cannot be studied experimentally. The necessity of studying a population of reactant ions introduces a statistical problem which is further complicated by the presence of the chemically inert but electrostatically active co-ions, which must always be present to satisfy the requirements of electrical neutrality of the solution. These complications can be eliminated in principle by determining the dependence of the rate upon the concentration of each ionic species present and extrapolating to infinite solution. Practically the procedure requires so much accurate data in the region of dilute solution

that it is unworkable. The Debye-Hückel theory, however, furnishes a valuable tool for estimating the effects of the surrounding ions of the medium under certain important limitations.

From a survey of the data available in 1922–4, Brönsted showed that there were three principal classes of kinetic anomalies and offered equations describing the behavior of each class.

(*a*) Primary salt effect, which is a pure kinetic effect resulting from the concentration dependence of electrostatic interactions of the type just described.

$$k = k_0 C_A C_B \frac{f_A f_B}{f_X}. \tag{4}$$

When the activity coefficients f of the ionic reactants and the critical complex X, whose algebraic net charge $Z_X = Z_A + Z_B$, is given by the Debye-Hückel limiting law

$$-\log f_i = 0.506 Z_i^2 \sqrt{\mu} \tag{5}$$

valid for water at 25° C., this equation assumes the limiting form valid for highly dilute solutions:

$$\log k = \log k_0 + 2Z_A Z_B (0.506)\sqrt{\mu}; \tag{6}$$

μ is the ionic strength.

(*b*) Secondary salt effect. This effect is produced by a shift in the degree of dissociation of a weak electrolyte furnishing one of the reactant ionic species. Electrostatic interaction produces this shift in equilibrium as shown in MacInnes' report.

If the reactant species is H^+ resulting from the dissociation of an acid $(HA)^{Z_{HA}} \rightleftharpoons B^{Z_B} + H^+$ into a base B of charge Z_B, then

$$C_{H^+} = K^0 \frac{C_{HA}}{C_B} \frac{f_{HA}}{f_B \cdot f_{H^+}}, \tag{7}$$

and since $Z_B = Z_{HA} - 1$, the Debye limiting law gives

$$C_{H^+} = K^0 \frac{C_{HA}}{C_B} \cdot 10^{Z_B} \tag{8}$$

as the quantity to be inserted in the classical kinetic equation for C_{H^+}.

(*c*) Generalized acid-base catalysis. Here catalysis is not restricted to H^+ or OH^- ions but is a property common to all acid or basic molecules, regardless of their electric charge type. For general acid catalysis,

$$\log k_a = \log G + \alpha \log K_A, \tag{9}$$

for general base catalysis,

$$\log k_b = \log G' + \beta \log K_B. \tag{10}$$

Here G and G' are constants depending primarily upon the substrate and temperature and to some extent upon the type of acid (or base). $K_A = 1/K_B$ is the dissociation constant of the conjugate acid-base catalytic system and α (or β) is a constant for any given substrate and acid-base system of the same charge type indicating the sensitivity of the substrate to acidic (or basic) catalysis.

PRIMARY SALT CATALYSIS.

Brönsted's formula for primary salt catalysis, $f_A f_B/f_X$, was developed originally on empirical and intuitive grounds. Bjerrum offered an exceedingly simple derivation, against which Brönsted offered a thermodynamic argument indicating the difficulties it encountered when applied to reversible reactions.[12] Bjerrum assumed that the collision complex X is in true equilibrium with A and B and that the rate is proportional to the concentration of critical complexes. From the thermodynamic relation, $C_X = KC_A C_B f_A f_B/f_X$, eq. (4) follows immediately from $k = k_3 C_X$.

The Brönsted and Bjerrum viewpoints may be reconciled in terms of the steady state process assumed by Christiansen:[3]

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_3} R. \tag{11}$$

In the steady state

$$\frac{dR}{dt} = \frac{(k_3 k_1) C_A \cdot C_B}{(k_2 + k_3)} = k_{obs} C_A \cdot C_B. \tag{12}$$

[12] La Mer: *Chem. Rev.*, **10**, 179 (1932).

If $k_2 \gg k_3$; k_{obs} reduces to $\frac{k_1}{k_2} k_3 = Kk_3$, the Bjerrum hypothesis. Skrabal calls X an Arrhenius intermediate. When $k_3 \gg k_2$ then $k_{obs} = k_1$. This is Brönsted's assumption and X corresponds to the type of intermediate postulated originally by van't Hoff to account for the fact that kinetic equations are often of lower order than the stoichimetric equation.[13]

For reactions which are slow enough to measure it seems reasonable to assume that $k_2 > k_3$, but the possibility of $k_3 > k_2$ cannot be arbitrarily ruled out. In Fig. 1 we give a summary of the best investigated reactions of different charge types.

The approach to the requirements of the limiting form of the Brönsted-Debye equation (6) for the primary salt effect with decreasing ionic strength is so striking for the various charge types of reactions shown in Fig. 1 that there can be little doubt of the fundamental validity of the Brönsted factor $f_A f_B / f_X$. The only significant question which remains appears to be how reliable are the Debye-Hückel equations for the behavior of activity coefficients in the complex mixtures encountered in kinetic measurements. La Mer and Fessenden [14] have shown that the same abnormalities which appear in the equilibrium case appear also in the kinetic case. In Fig. 2 we exhibit the behavior of log k for the bromoacetate-thiosulfate ion replacement reaction:

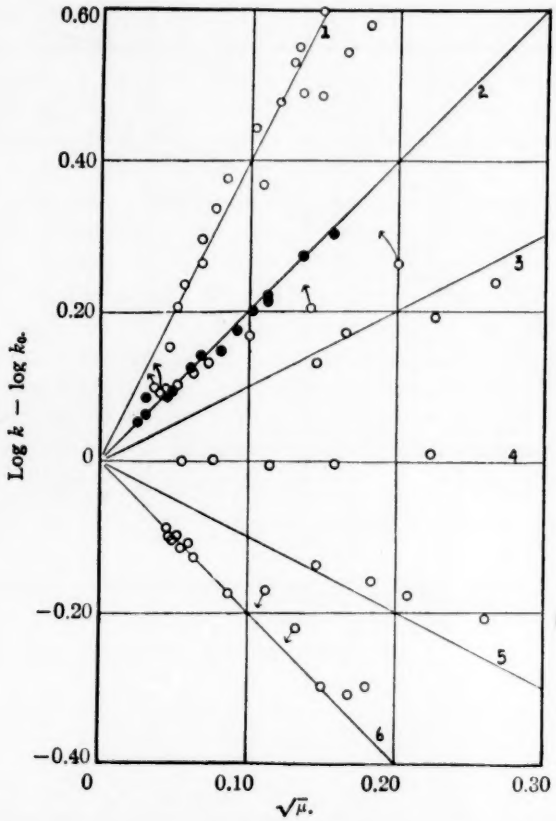
$$BrCH_2COO^- + S_2O_3^= \rightleftharpoons X^= \rightarrow S_2O_3CH_2COO^= + Br^-.$$

This reaction has been intensively studied in the laboratories at Columbia University since 1929. It is almost unique in its freedom from side reactions and the precision and accuracy with which its rate can be followed in highly dilute solutions. When Na^+ or K^+ is the co-ion the Debye-Hückel first approximation equation is obeyed; when the co-ion is Ba^{++}, Mg^{++}, or Ca^{++} the limiting law is not obeyed at least within the limits of dilution that permit of accurate measurement. In Fig. 3 we plot the activity coefficients of a tri-

[13] Schwab: Catalysis. Translated by Taylor and Spence. Van Nostrand, 1937, pp. 71–75, 137–148. This book treats this problem in considerable detail.

[14] La Mer and Fessenden: *J. Am. Chem. Soc.*, **54**, 2351 (1932).

FIG. 1.



The influence of ionic strength on the velocity of the ionic reactions.

1. $2(Co(NH_3)_5Br)^{++} + Hg^{++} + 2H_2O \rightarrow 2(Co(NH_3)_5H_2O)^{+++} + HgBr_2$ (Bimolecular). No foreign salt added. Brönsted and Livingston: *J. Am. Chem. Soc.*, **49**, 435 (1927).

2. Circles. $CH_2BrCOO^- + S_2O_3^{--} \rightarrow CH_2S_2O_3COO^- + Br^-$ as the sodium salt. No foreign salt added. La Mer: *J. Am. Chem. Soc.*, **51**, 334 (1929).

Dots. $S_2O_8^{--} + I^- \rightarrow I_2 + SO_4^{--}$ as $Na_2S_2O_8$ and KI. King and Jacobs: *J. Am. Chem. Soc.*, **53**, 1704 (1931).

3. Saponification of nitrourethane ion by hydroxyl ion. $(NO_2 = N - COOC_2H_5)^{--} + OH^- \rightarrow N_2O + CO_3^{--} + C_2H_5OH$. Brönsted and Delbanco: *Z. anorg. Chem.*, **144**, 248 (1925).

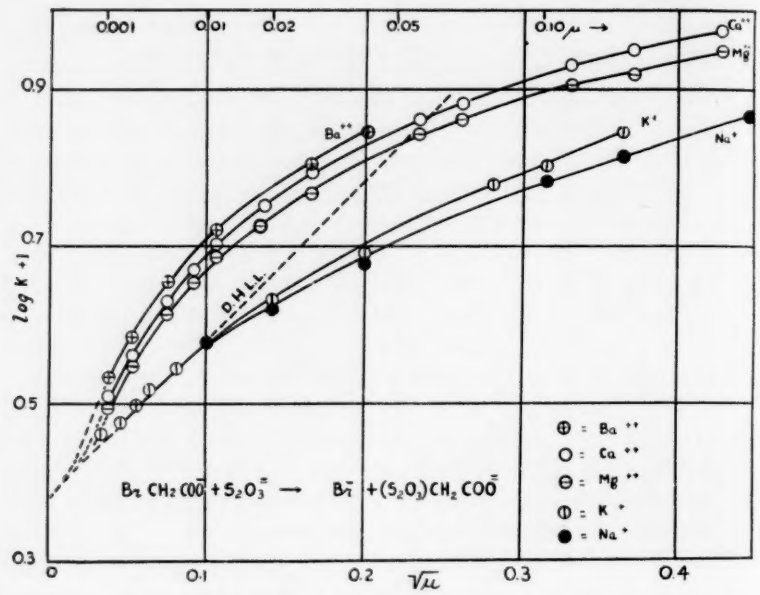
4. $C_{12}H_{22}O_{11}^0 + OH^- \rightarrow$ Invert Sugar. Arrhenius: *Z. physik. Chem.*, **1**, 111 (1887).

5. $H_2O_2 + H^+ + Br^- \rightarrow H_2O + Br_2$. Livingston: *J. Am. Chem. Soc.*, **48**, 53 (1926).

6. $(Co(NH_3)_5Br)^{++} + OH^- \rightarrow (Co(NH_3)_5OH)^{++} + Br^-$. Brönsted and Livingston: *J. Am. Chem. Soc.*, **49**, 435 (1927).

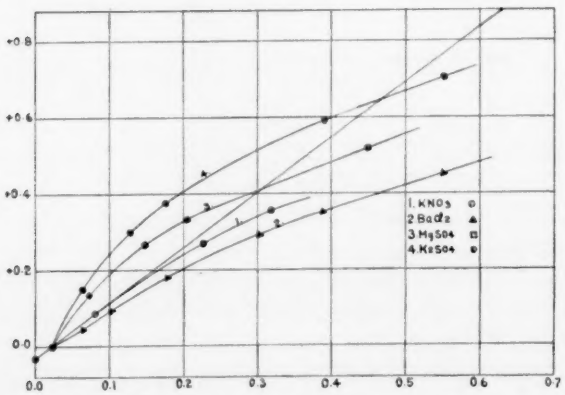
A large number of reactions corresponding to the type $A^+ + B^0 \rightleftarrows (X)^+$ yielding a linear salt effect are to be found in the studies of Harned and Åkerlof, and Brönsted and his collaborators. See *J. Am. Chem. Soc.*, **50**, 358 (1928); **51**, 248 (1929); *Trans. Faraday Soc.*, **25**, 59 (1929).

FIG. 2.



The influence of divalent cations as contrasted with monovalent cations on the velocity of the bromoacetate-thiosulfate reaction as a function of the ionic strength.

FIG. 3.



The activity coefficient of a tri-univalent cobalt amine as determined by solubility measurements showing the deviations from the Debye-Hückel limiting law when the ion of sign opposite to the trivalent cation solute is of valence greater than unity.

univalent cobalt ammine as determined by La Mer and Mason [15] from solubility measurements.

When the anion of sign opposite to the trivalent positive cation is univalent (NO_3^- or Cl^-), the Debye-Hückel first approximation is obeyed. When the anion is of higher valence ($SO_4^=$, $Fe(CN)_6^=$, $Fe(CN)_6^{\equiv}$), the Debye theory is no longer applicable. The marked similarity between the kinetic data of Fig. 2 and the thermodynamic data of Fig. 3 shows clearly that the abnormalities appear in water when the numerical products of the valences of the ions of opposite sign exceed 3. Since the factor Z_1Z_2/Da is the principal factor in determining the range of validity of the Debye theory it is evident that increasing Z_1Z_2, the product of the charges of ions of opposite sign, from 1 to 3 is equivalent to reducing D from 78 to 78/3. This problem is considered in detail by Tomlinson and La Mer in a paper which will appear shortly.

The electrostatic theory [1, 2, 3, 4, 5] for the rate of an ionic reaction of the type

$$A^{Z_A} + B^{Z_B} \rightleftarrows X^{Z_X} \rightarrow R, \qquad (13)$$

where X is the critical or transition state and the superscript Z refers to the sign and number of electric charges on the ions may be epitomized in the equation: [4]

$$\log k = \log k_0 - \frac{Z_A Z_B \epsilon^2 N}{DRT} \cdot \frac{1}{(r_A + r_B)} + \frac{Z_A Z_B \epsilon^2 N}{DRT} \cdot \frac{\kappa}{1 + a\kappa}. \qquad (14)$$

Here k_0 is the molar rate constant extrapolated to a medium of dielectric constant $D = \infty$, in which medium all electrostatic effects derived from Coulomb's law vanish. The last term accounts for the Bronsted primary salt effect calculated from the Debye-Hückel approximation for the electric potential of an ion against its ionic atmosphere.

Extrapolation of the observed values of $\log k$ as a function of Debye's $\kappa = \sqrt{\frac{4\pi\epsilon^2 N}{DRT} \Sigma c_i z_i^2}$, to κ = zero; i.e. to zero ionic strengths, yields $\log k_0^D$, the molar rate constant freed from the catalytic effect of the surrounding atmosphere of ions and

[15] La Mer and Mason: *J. Am. Chem. Soc.*, **49**, 410, 363 (1927).

valid for the solvent of dielectric constant D. From the constancy of the parameter a as a function of κ, or conversely the constancy of $\log k_0^D$ for an assigned a, one can determine the range (concentration) of validity of the Debye approximation for a given D and type of ions involved.

The remaining term is the kinetic counterpart of the Born equation for the work of transforming an ion from a medium $D = \infty$ to the given medium when applied to the activation process in eq. (11). This term arises from the electric potentials of the respective ions by virtue of their charges in the absence of an ion atmosphere ($\kappa = 0$). For reactions between ions of the same sign the absolute rate ($\log k_0$) is reduced as a result of the repulsive effect of the charges on the reactants, and conversely for ions of opposite sign.

In the Christiansen-Scatchard derivation (refs. 3, 4) the distance of closest approach of a central ion to the average centers of the ion atmosphere averaged for the two reactant ions as central ions is taken as equal to the distance of closest approach of the centers of the two reacting ions. In other words $a = r_A + r_B$ where r = radius. It is a matter of considerable interest therefore to determine $(r_A + r_B)$ from the slope of $\log k_0^D$ *vs.* $1/D$ and to compare the result with that obtained from the kappa (interaction with the ionic atmosphere) function.

In their report of the influence of the addition of non-electrolytes upon the kinetics of the bromoacetate-thiosulfate reaction La Mer and Kamner [16] mentioned that no simple relation existed between their values of $\log k$ and $1/D$ when the concentrations ranged between $m = 0.002$ to 0.05 and D extended from 88.4 (21 per cent. urea) to 33 (50 per cent. dioxane); the same was true of Kappana's [17] data in which aqueous ethyl alcohol was used as solvent. The addition of non-electrolytes increased the rate in spite of decreasing the dielectric constant. Eagle and Warner [18] have since pointed out that if the comparison is made with the $\log k_0^D$ values extrapolated on the assumption that the Debye-Hückel function ($a = 5.6$ Å) is valid in solvents other than water that

[16] La Mer and Kamner: *J. Am. Chem. Soc.*, **57**, 2669 (1935). See p. 2672.
[17] Kappana: *J. Ind. Chem. Soc.*, **6**, 419 (1929).
[18] Eagle and Warner: *J. Am. Chem. Soc.*, **58**, 2335 (1936).

these data and particularly those of Staup-Cope and Cohn [19] which appeared simultaneously with those of La Mer and Kamner, and which involve higher dielectrics (D = 78 to 100), are in better agreement with the requirements of eq. (14) than would be implied from the highly abbreviated comment of La Mer and Kamner. Eagle and Warner's evidence can hardly be accepted as proving eq. (14) particularly since they omit all data for $D < 50.3$ on their plot. Since Staup-Cope and Cohn also encountered difficulty in harmonizing Kappana's data with the requirements of the simple electrostatic theory, Tomlinson and La Mer (in press) have extended the kinetic measurements on this reaction to D = 141, by the addition of 2.8 molar glycine, and to D = 50, 30 and 20, by additions of tertiary butyl alcohol and of 1–4 dioxane. The latter were chosen since their isodielectric mixtures are of comparable water content.

The constancy of $\log k_0^D$ over the concentration range $\sqrt{\mu}$ = 0.089 to 0.365 (Table I) furnishes ample evidence of the high precision with which the Debye approximation reproduces the experimental data when $D \geq 70$. The value of $(2 + \log k_0^D)$ given in the column (11) is the average value

TABLE I.

The Constancy of log k_0^D Calculated by Use of Eq. (14) at Various Ionic Strengths as a Test of the Brönsted-Debye Interaction Term.

Cation.	Solvent.	t.	D.	$\sqrt{\mu}$.	0.089.	0.141.	0.283.	0.365.	Parameter.	Av. log $k_0^D + 2$.	Observer.
K^+	H_2O	25°	78.54	$2 + \log k_0^D$	1.399	1.405	1.400	1.401	5.6 Å	1.399	F
Na^+	H_2O	25	78.54	$2 + \log k_0^D$	1.403	1.400	1.400	1.400	6.4 Å 6.3 Å	1.399 1.401	F K
Na^+	H_2O	0	88.36	$2 + \log k_0^D$	0.344	0.340	0.340	0.345	6.2 Å	0.343	K
Na^+	sucrose	25	70.0	$2 + \log k_0^D$	1.368	1.367	1.365	1.366	6.5 Å	1.366	K
Na^+	sucrose	0	78.4	$2 + \log k_0^D$	0.324	0.322	0.323	0.321	6.5 Å	0.323	K

When $\sqrt{\mu}$ = 0.447 is produced by the addition of 0.18M NaCl, $\log k_0^D$ = 9.401–10 (a = 5.70 Å) at 25° C. and 8.343–10 (a = 5.54 Å) at 0° C.

K = Kamner; F = Fessenden.

[19] Staup-Cope and Cohn: *J. Am. Chem. Soc.*, **57**, 1794 (1935). See p. 1797 and footnotes.

TABLE II.

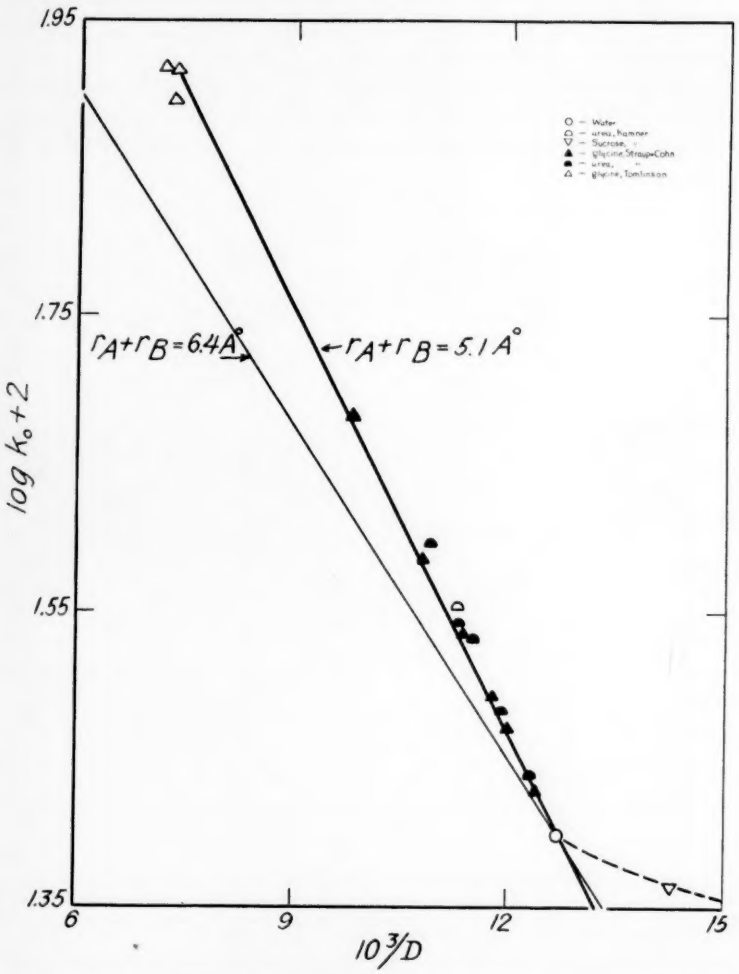
Reaction.	Ionic Type.		P (observed).	r in Å (calc.).
	Z_A	Z_B		
$Cr(H_2O)_6^{+++} + CNS^-$	+3	−1	$1.09 \times 10^{+8}$	1.67
$Co(NH_3)Br^{++} + OH^-$	+2	−1	$1.39 \times 10^{+6}$	1.37
$NH_4^+ + CNO^-$	+1	−1	$3.83 \times 10^{+1}$	3.48
$XH^+ \times Br^-$	+1	−1	$2.46 \times 10^{+1}$	3.85
$XH^+ + Cl^-$	+1	−1	$4.76 \times 10^{+1}$	2.98
$ClO^- + ClO^-$	−1	−1	3.19×10^{-3}	1.60
$ClO^- + ClO_2^-$	−1	−1	2.83×10^{-3}	1.57
$C_6H_5 \cdot C : C \cdot COO^- + I_3^-$	−1	−1	4.83×10^{-4}	1.28
$CH_2Cl \cdot COO^- + S_2O_3^{--}$	−1	−2	3.92×10^{-5}	1.85
$CH_2Br \cdot COO^- + S_2O_3^{--}$	−1	−2	7.64×10^{-3}	3.66
$Co(NH_3)Br^{++} + Hg^{++}$	+2	+2	4.30×10^{-4}	5.57
$AsO_3^{--} + TeO_4^{--}$	−2	−2	6.77×10^{-6}	3.10
$S_2O_4^{--} + S_2O_4^{--}$	−2	−2	6.07×10^{-8}	1.96

for all of the data of that observer for the assigned value of the parameter a. a is known to $\pm$ 0.1 Å for each set of data; an increase of 0.1 Å increases $\log k_0^D$ by 0.0035 at $\sqrt{\mu} = 0.365$.

The value $a = 5.6$ Å employed by Eagle and Warner appears to be restricted to potassium as the chemically inert cation. When the cation is sodium, $a = 6.3$ to 6.4 Å. It is significant that a is not perceptibly affected by temperature (0 to 25° C.) or by the addition of 32.4 per cent. sucrose for univalent cations.

In figure 4, the most reliable values of $\log k_0^D$ for $D > 70$ are plotted against $1/D$. The functional agreement with equation 2 is excellent but the parameter $r_A + r_B = 5.1$ Å instead of 6.4 Å. Since there is no uncertainty in the extrapolation in 32.4 per cent. sucrose, the sharp change in slope between $D = 78.54$ and $D = 70$ produced by the addition of this non-polar solute must be recognized as a real effect which is clearly incompatible with equation 14. The sharp change in slope is pronounced for the experimental $\log k$ data in fig. 5, particularly for the concentration $a = b = 0.005$ M. At $D = 50$ the Debye function is no longer strictly valid but a graphical extrapolation to $\mu = 0$ yields $\log k_0^D = 9.200 - 10$ with an uncertainty of $\pm$ 0.010. On the other hand when $D = 30$, $\log k$ is determined predominantly by terms of higher order than the Debye approxima-

FIG. 4.



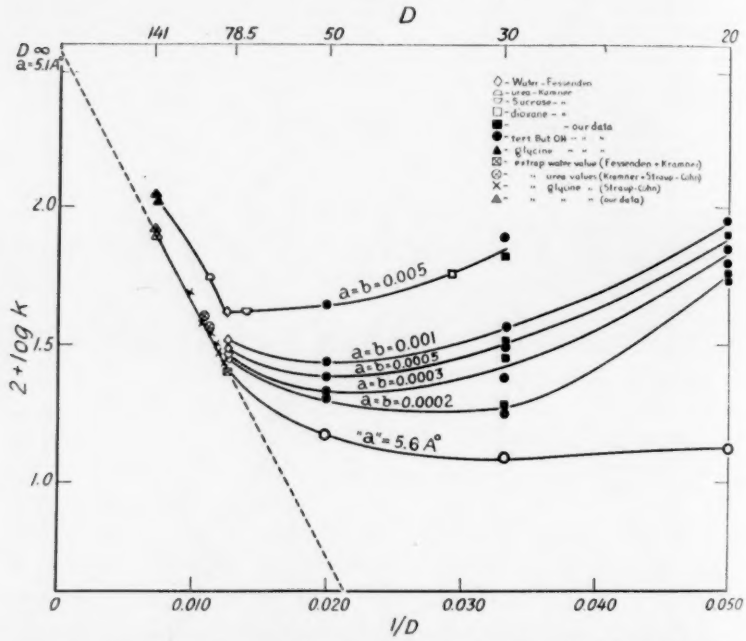
The dependence of log k_0 for the bromoacetate-thiosulfate reaction as a function of $1/D$ in high dielectric solvents.

tion, and the form of the curves is similar to those calculated in the extended theory of La Mer, Gronwall and Greiff [20] for the activity coefficient of a single electrolyte of unsymmetric valence type.

[20] La Mer, Gronwall and Greiff: *Jour. Phys. Chem.*, **35**, 2245 (1931).

Unfortunately when the attempt was made to apply this extended theory to the complicated problem at hand, the 3rd and 4th power terms of the type $(Z_A^3 + Z_B^3 - (Z_A + Z_B)^3)$ became so sensitive to the individual values of the parameter employed for each possible ion-pair in the system that a calculation using an average value of a is not sufficiently

FIG. 5.



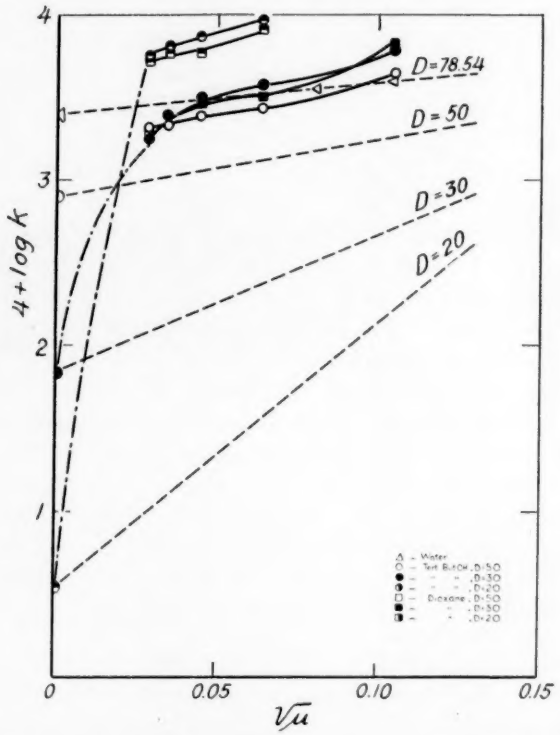
The dependence of the observed velocity constant (log k) as a function of $1/D$ for high and low dielectric solvents. Filled circles, tertiary butyl alcohol; filled squares, dioxane; circles, extrapolated values for A = 5.6 Å; filled triangles, glycine; lozenges, water; crosses, urea (from Staup-Cope and Kamner). Data by La Mer, Tomlinson and Kamner.

convincing to warrant the tedious calculations. A graphical extrapolation for log k_0^D indicates a value of 8.70 − 10 for $\mu = 0$. Eq. (14), however, demands a value of log k_0 = 7.84 − 10 for $r_A + r_B$ = 6.4 Å. The extent of the discrepancy between eq. (14) and any graphical extrapolation are shown clearly in Fig. 6.

For a mixed solvent the more polarizable molecules (glycine) will accumulate around the ions and the less polarizable

molecules (H_2O) will be repelled. The effective dielectric constant between the reacting ions which should be employed in eq. (14) will accordingly be greater than the average bulk dielectric which is actually measured and plotted as the abscissa in Figs. 4 and 5.

FIG. 6.



The character of the extrapolations to infinite dilution necessary to obtain agreement with equation 14.

The use of macroscopic dielectric constants is possibly the explanation for the 25 per cent. difference in slope in Fig. 4, when $D > 78$, represented by $r_A + r_B = 5.1$ Å and $a = 6.4$ Å. A further decrease in slope of comparable magnitude should be expected when a less polarizable component (sucrose, alcohol, or dioxane) is added to reduce D below 78, since now water rather than the non-electrolyte will accumu-

late preferentially around the ion. The *progressively decreasing* slopes observed with decreasing D, however, can hardly be explained on this basis alone.

In low dielectric solvents, the mutual electrostatic energy between oppositely charged ions exceeds their translatory energy with the result that on a time average these ions exist predominantly as associated clusters. In the terminology of Bjerrum and Fuoss and Kraus this phenomenon is called ion-association (see report by Kraus). As was pointed out by La Mer and Kamner [16] when $D \sim 50$, the sodium and thiosulfate ions exist primarily as $(NaS_2O_3)^-$. The reaction is therefore predominantly between $BrAc^- + NaS_2O_3^-$; $Z_A Z_B = 1$ and the slope of $\log k_0^D$ *vs.* $1/D$ should be ½ of its value at higher dielectrics. At sufficiently low dielectrics, the principal species will be NaBrAc and $Na_2S_2O_3$, and the slope will be zero. This situation is approached at $D = 30$.

The extrapolation to $D = \infty$ in Fig. 4 yields $\log k_0 = 0.56$ or $k_0 = 3.6$. This value should approximate the rate of reaction between thiosulfate ion and the uncharged methyl ester,[21] if no significant change in reactivity is produced when the charge of bromoacetate is eliminated by the substitution of the methyl ester. The earlier [22] value of 13.3 in H_2O is confirmed. However this rate is doubled, $k = 27$, in a butyl alcohol mixture $D = 20$. In glycine k varied from 7 to 14. Exact agreement with equation (2) cannot be expected since dipole forces operate between a neutral molecule and an ion.

Substitution of $k_{ester} = 13.3$ in the equation

$$\log \left(\frac{k_{ester}}{k_{ion}} \right)_{\mu=0} = \frac{Z_A Z_B \, 3.06.10^{-8}}{(r_A + r_B)}, \qquad (15)$$

derived from equation (14), yields $r_A + r_B = 3.52$ Å (H_2O). Slator's data [23] for the ethyl chloracetate-thio reaction ($\log k_0 = 9.14-10$) and Krapiwin's extrapolated value [24] for the chloracetate-thio reaction ($\log k_0 = 7.36-10$; $a = 6$ Å) yield $r_A + r_B = 3.4$ Å. All of these values are physically reasonable.

[21] La Mer: *Chem. Review* (ref. 12).
[22] La Mer and Kamner: *J. Am. Chem. Soc.*, **53**, 2833 (1931).
[23] Slator: *J. Chem. Soc.*, **87**, 481 (1905).
[24] Krapiwin: *J. Chim. Phys.*, **10**, 287 (1912).

Eq. (14) may be tested in still another way. One can assume that the absolute rate of reaction for uncharged molecules is given by the collision theory $k_0 = ZPe^{-E/RT}$. E is determined by the Arrhenius equation from values of log k_0^D and an expression for P is set up in terms of $r_A + r_B$ by a method to be described in the next chapter. Table II gives the calculations of Moelwyn-Hughes.[25] As this author states, "some of the data quoted here suffer because no systematic allowance can be made for the simultaneous effect of temperature, ionic strength and concurrent reactions." When we recognize that the collision theory frequently fails[26] to predict the velocity of uncharged molecules by factors ranging from 10^{-2} to 10^{-8}, it is obvious that a strict interpretation of $r = r_A + r_B$ cannot be made. Nevertheless the fact that values of $r = 1.67$ and 1.96 can account for a total change in rate of 10^{16} simply on the basis of Coulomb's law and the charge type furnishes convincing evidence of the fundamental validity of the electrostatic theory of kinetics. The negative values of r encountered in some cases with Moelwyn-Hughes treatment are presumably due to the use of log Z instead of log (kT/h). See eqs. (21) and (26) below.

ADDITIONS OF LANTHANUM SALTS.

The addition of 0.001 M La^{+++} (Fig. 7) in the form of $LaCl_3$ to the reactants bromoacetate and thiosulfate ions at low concentration in water produced a 7 to 9 fold increase in rate which far exceeded the predictions of the Debye-Hückel theory. When $D = 20$, minute La^{+++} additions exert a tremendous catalytic effect (Fig. 8), which passes through a maximum representing a 200 fold increase in rate. The maximum rate log $k = 2.225$ exceeds the rate predicted for $D = \infty$ by 1.67 logarithmic units.

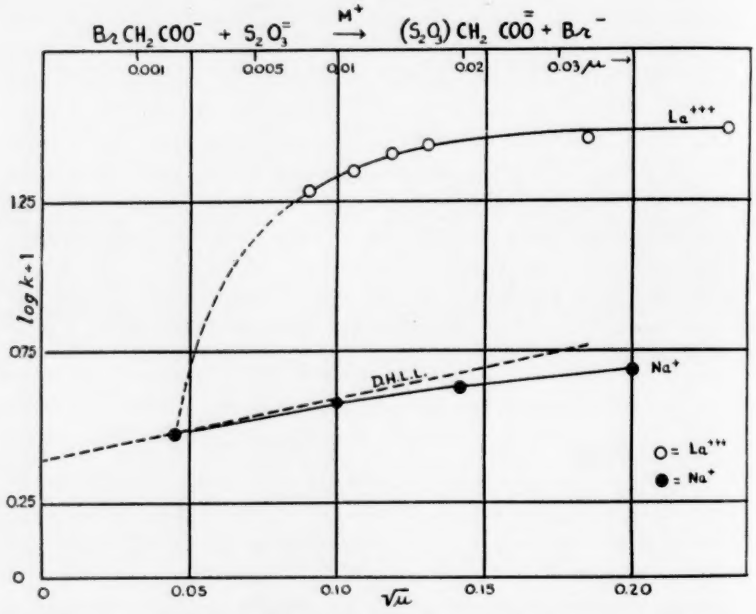
The extent of ion-association between oppositely charged ions (1) and (2) depends upon the factor $\frac{Z_1 Z_2 N\epsilon^2}{DRTa}$. Since $Z_1 = 3(La^{+++})$ and $Z_2 = -2(S_2O_3^{=})$ and D is reduced to $\frac{1}{4}$ of its value in water, each La^{+++} ion can hold a thiosulfate

[25] Moelwyn-Hughes: *Proc. Roy. Soc. A.*, **155**, p. 308 (1936).

[26] Moelwyn-Hughes: Kinetics of Reactions in Solution, Oxford Press, 1933 (p. 111).

ion very firmly as $(LaS_2O_3)^+$ and still attract a bromoacetate ion to form a stable uncharged reactive triplet. The number of triplets will increase with increasing La^{+++} concentration until the charges upon the La^{+++} are substantially neutralized by association with the reactants. Above this critical concentration, the rate should decrease since the excess La^{+++} will present so many competing and widely spaced attractive

FIG. 7.

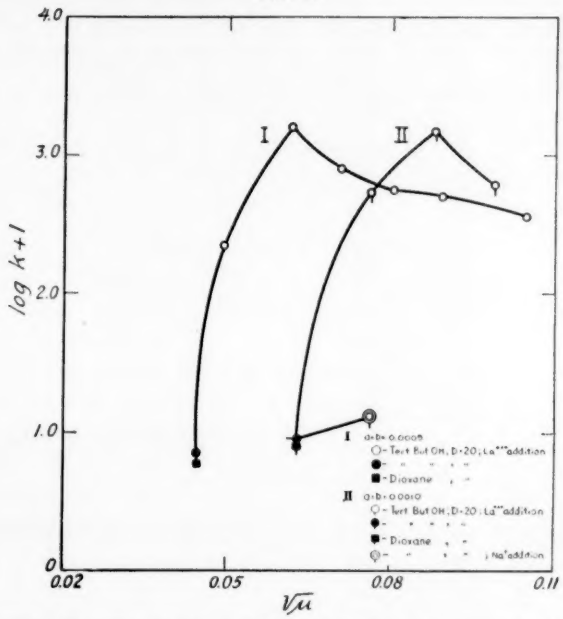


The marked accelerating influence of lanthanum ion additions upon the bromoacetate-thiosulfate reaction in water. Data by La Mer and Fessenden.

centers to the negative reactants that the frequency of contact of reactants is reduced.

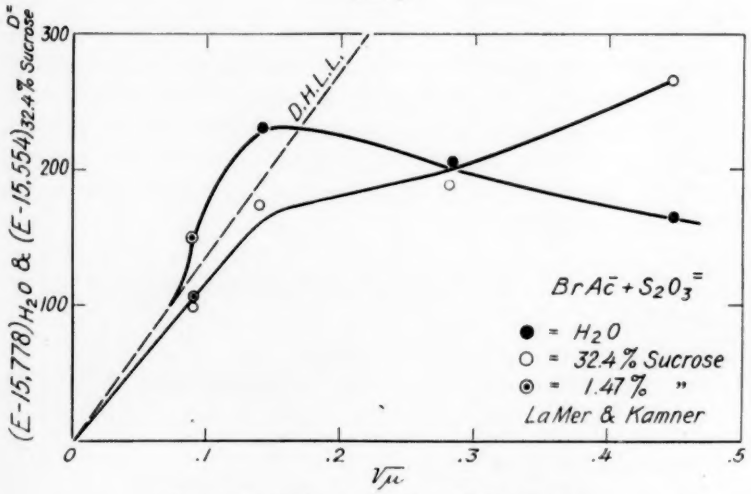
This explanation is supported by the data. 0.62 MM of La^{+++} produce approximately the same rate when added to 1 MM of reactants as 0.30 MM addition of La^{+++} produces upon a 0.5 MM concentration of reactants. MM = 10^{-3} M. The critical ratio La^{+++}/reactants appears to be 0.6. The effect of additions of NaCl is relatively small, although greater for $D = 20$ than for $D = 78$. The ratio of the molar cata-

FIG. 8.



The marked accelerating effect of minute additions of lanthanum ion upon the kinetics of the bromoacetate-thiosulfate ion reaction. Data by La Mer and Tomlinson. $D = 20$.

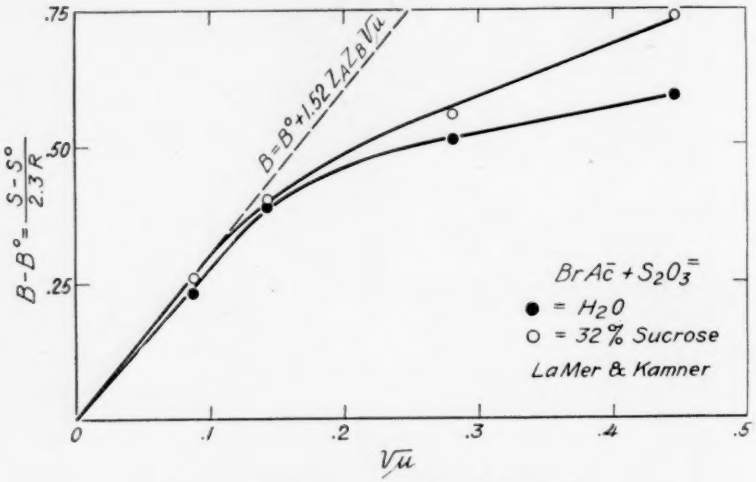
FIG. 9.



Energy of activation as a function of ionic strength.

lytic constants for La^{+++} and Na^{+} ions compared at the ionic strength yielding the maximum effect noted for La^{+++}, is approximately 2200. This ratio remains practically unchanged on passing from $D = 20$ to $D = 30$.

FIG. 10.



Entropy of activation as a function of ionic strength.

EFFECTS OF TEMPERATURE.

Within the past five years it has been shown [27–30] that significant progress can be achieved in the field of reaction kinetics if one assumes that the critical complex is in equilibrium with the reactants and that the rate of reaction depends only upon the frequency with which the molecules leave the critical state; i.e. pass over the energy barrier. Denoting this frequency by ν we have

$$\frac{dR}{dt} = \nu C_X = \nu K C_A C_B \qquad (16)$$

or for unit concentrations of reactants

$$k = \nu K. \qquad (17)$$

[27] La Mer: *J. Chem. Physics*, **1**, 289 (1933).
[28] Rodebush: *ibid.*, **1**, 440 (1933).
[29] Rice and Gershinowitz: *ibid.*, **2**, 853 (1934).
[30] Eyring: *ibid.*, **3**, 107 (1935); *Chem. Rev.*, **17**, 65 (1935).

Since the equilibrium constant K for the activation process $A + B \rightleftarrows X$ is related to the increase in the standard free energy ΔF^* by the relation

$$\Delta F^* = - RT \ln K, \tag{18}$$

the velocity constant of reaction becomes

$$k = \nu e^{-\Delta F^*/RT}. \tag{19}$$

By employing the thermodynamic operators

$$S = \frac{-\partial F}{\partial T} \qquad \text{and} \qquad E + PV = \frac{\partial (F/T)}{\partial (1/T)}$$

to decompose F into its components $(E + PV) - TS$, where S is entropy and E is internal energy, the kinetic eq. (18) neglecting the minor term in PV becomes

$$k = \nu e^{\Delta S^*/R} e^{-\Delta E^*/RT}. \tag{20}$$

In La Mer's treatment (ref. 27), based upon Tolman's statistical development of the Arrhenius equation, ν was set equal to Z^0, the collision number (eq. 1), and the entropy of activation was denoted by S_{act}.

In a more recent paper Eyring (ref. 30) has shown by an elegant statistical argument that $\nu = kT/h = RT/Nh$; i.e. to a universal frequency proportional to the absolute temperature. In Eyring's treatment ΔS^* contains the entropy contributions of all degrees of freedom (translation and internal), whereas in La Mer's entropy of activation, S_{act}, the contribution of the two translational degrees of freedom entering into the collision process are contained in Z^0. It does not seem to be generally appreciated that Z^0 is composed of the product of a pure frequency and the entropy contribution of two translation degrees of freedom.

In the notation of the English School

$$k = PZ^0 e^{-E/RT}. \tag{21}$$

Here P is called a probability factor but is obviously related to La Mer's entropy of activation by the relation

$$\log P = S_{\text{act}}/2.3R. \tag{22}$$

These quantities are related to the empirical integrated form

of the Arrhenius equation; namely

$$k = \alpha e^{-E/RT}, \tag{23}$$

$$\log k = B - E/RT, \tag{24}$$

where $\log \alpha = B$ (the frequency factor), by the relations

$$B = \log\left(\frac{kT}{h}\right) + \frac{\Delta S^*}{2.3R} - \frac{\Delta E^*}{2.3RT} \tag{25}$$

$$= \log Z^0 + \frac{S_{act}}{2.3R} - \frac{\Delta E^*}{2.3RT}. \tag{26}$$

With this introduction we can consider more profitably the effects of temperature upon the primary salt effect.

Multiply each term of eq. (14) by $RT/2.303$; then

$$RT \ln k = RT \ln k_0 - \frac{Z_A Z_B N \epsilon^2}{D} \frac{1}{(r_A + r_B)} + \frac{Z_A Z_B N \epsilon^2}{D} \frac{\kappa}{1 + a\kappa}. \tag{27}$$

Subtracting $RT \ln \nu$ from both sides and changing signs yields (27) in terms of the free energy of activation

$$\Delta F^* = \Delta F_0^* + \Delta F_D^* + \Delta F^*_{\text{interaction}} \tag{28}$$

as a compact method of referring to the terms in eq. (27).

Decomposing the free energy of activation ΔF^* into its components $\Delta H^* - T\Delta S^*$ by the thermodynamic operators used in eq. (20) and neglecting the unimportant PV term in $H = E + PV$,

$$\Delta E^* = \Delta E_0^* + \Delta E_D^* + \Delta E^*_{\text{interaction}}, \tag{29}$$

$$\Delta S^* = \Delta S_0^* + \Delta S_D^* + \Delta S^*_{\text{interaction}}. \tag{30}$$

ΔE_0^* and ΔS_0^* are obviously the energy and entropy of activation of the process $A + B \rightleftarrows X$ for the uncharged molecules or for the ions at $D = \infty$. The dependence of ΔF_D^* upon $1/D$ yields the simple relations

$$\Delta E_D^* = \Delta F_D^* \left[1 + \frac{T}{D}\frac{\partial D}{\partial T}\right], \tag{31}$$

$$\Delta S_D^* = \Delta S_D^* \left[\frac{T}{D} \frac{\partial D}{\partial T} \right]. \tag{32}$$

The interaction term in its limiting form varies as $(D^{-3/2} V^{-1/2} T^{-1/2})$ since κ varies as $(DVT)^{-1/2}$. Hence when $a\kappa$ can be neglected in respect to unity (Limiting Law),[31]

$$\Delta E^*_{in} = \frac{3}{2} \Delta F^*_{in} \left[1 + \frac{T}{D} \frac{\partial D}{\partial T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T} \right], \tag{33}$$

$$\Delta S^*_{in} = \frac{3}{2} \frac{\Delta F^*_{in}}{T} \left[\frac{1}{3} + \frac{T}{D} \frac{\partial D}{\partial T} + \frac{1}{3} \frac{T}{V} \frac{\partial V}{\partial T} \right]. \tag{34}$$

When $a\kappa$ cannot be neglected, but neglecting terms in $\partial V/\partial T$, then for the interaction terms

$$\Delta E^*_{in} = \frac{3}{2} \Delta F^*_{in} \left[\frac{\left(1 + \frac{2}{3} a\kappa \right)}{(1 + a\kappa)} \left(1 + \frac{T}{D} \frac{\partial D}{\partial T} \right) \right], \tag{35}$$

$$\Delta S^*_{in} = \frac{3}{2} \frac{\Delta F^*_{in}}{T} \left[\left(\frac{1}{3} + \frac{T}{D} \frac{\partial D}{\partial T} \right) - \frac{1}{3} \left(\frac{a\kappa}{1 + a\kappa} \right) \left(1 + \frac{T}{D} \frac{\partial D}{\partial T} \right) \right]. \tag{36}$$

For water at 25° C. $(T/D)(\partial D/\partial T) = -1.37$; hence, the factors in eqs. (35) and (36) become respectively -0.37 and -1.04.

Since

$$\frac{\Delta F^*}{2.3RT} = -2Z_A Z_B (0.506) \sqrt{\mu}, \tag{37}$$

the limiting laws for the dependence of ΔE^* and ΔS^* upon the ionic strength assume the following simple forms:[31]

$$\frac{\Delta \mu \Delta E^*}{2.3RT} = \frac{\Delta E^* - \Delta E_0^*}{2.3RT} = 0.51 Z_A Z_B \sqrt{\mu}, \tag{38}$$

$$\frac{\Delta \mu \Delta S^*}{2.3R} = \frac{\Delta S^* - \Delta S_0^*}{2.3R} = B - B^0 = 1.52 Z_A Z_B \sqrt{\mu}. \tag{39}$$

[31] La Mer and Kamner: *J. Am. Chem. Soc.*, **57**, 2662 (Dec., 1935). Eqs. (5) to (13). Eq. (33) is strictly an expression for ΔH^*. When the minor term in $\partial V/\partial T$ is omitted, eq. (33) is an exact expression for ΔE^*.

Equations (33) and (34) are exact forms of the Debye-Hückel theory but in equations (35) and (36) the tacit assumption that $\left(\frac{\partial D}{\partial T}\right)_{\kappa=0}$ equals $\left(\frac{\partial D}{\partial T}\right)_{\epsilon}$ is probably not true. Unfortunately no theory has appeared which is competent to describe the concentration behavior of $\left(\frac{\partial D}{\partial T}\right)$. The reader is referred to papers on the heats of dilution where this problem has been discussed.[32, 33] The electrostatic contribution to the energy of activation is simply the heat of dilution for the process $A + B \rightleftarrows X$; i.e. $\Delta E^* = \bar{L}_X - (\bar{L}_A + \bar{L}_B)$, where $\bar{L}$ is the relative partial molal heat content.

The most striking feature of the heat of dilution is the persistence to low concentration of specific individual properties of the electrolyte as contrasted with the free energy results, and the frequent change in sign of the heat of dilution at the moderate concentration $\sqrt{\mu} = 0.2$ to 0.4.

THE BROMOPHENOL BLUE REACTION.

Panepinto and Kilpatrick[34] have shown very recently that the fading of the tetrahalogen derivatives of the sulfonphthalein dyes by NaOH is an ionic reaction in which OH^- ion replaces a bromine atom in the divalent negative dye ion. For bromphenol blue (Br ϕ B),

$$\mathrm{Br}\,\phi\,\mathrm{B}^{=} + \mathrm{OH}^- \rightleftarrows X^{=} \rightarrow (\mathrm{OH}\,\phi\,\mathrm{B})^{=} + \mathrm{Br}^-;$$

we have a reaction of precisely the same type as the bromoacetate-thiosulfate reaction discussed above. These authors find that log k at 20, 25 and 30° C. obeys the Brönsted-Debye primary salt equation for $\mu = 0.001$ to 0.2, approaching a limiting slope corresponding to $Z_A Z_B = 2$, which they properly accept as good evidence for the postulated ionic mechanism. The concentration of dye is fixed at 2.10^{-5} M and the variation of ionic strength is produced by NaOH addi-

[32] La Mer: Annual Survey of American Chemistry, V (1930), pp. 12–13; La Mer and Parks: *J. A. C. S.*, **55**, 4343 (1933), pp. 4352–3; Shrawder and Cowperthwaite: *ibid.*, **56**, 2345 (1934).

[33] Lange and Robinson: *Chem. Revs.*, **9**, 89 (1931), and the report of Harned at this Symposium.

[34] Panepinto and Kilpatrick: *J. Am. Chem. Soc.*, **59**, 1871 (1937).

tions. Although the authors recognize that their data are not sufficiently accurate to test the effects of *temperature* upon the energy of activation, they claim that the effect of ionic strength upon the energy of activation is not in agreement with the equations developed by Moelwyn-Hughes.[35, 36]

Panepinto and Kilpatrick apparently are not aware that the equations of Moelwyn-Hughes are substantially identical with the equations (33) and (34) published in 1935 by La Mer and Kamner in The Journal of The American Chemical Society when proper recognition of the difference in notation and terminology between the English and American Schools is taken into account. Panepinto and Kilpatrick's deduction that their values of E and of P do not obey eqs. (33) to (36) over the range $\mu = 0.001$ to 0.2 is of course as surprising as it is important. It means that their data obey the electrostatic theory in the form of the free energy but fail to obey relations based on the same premises when presented in the form of the internal energy and entropy of activation.

We offer three possible explanations: (*a*) the quasi-thermodynamic treatment of kinetics, eqs. (11) and (12), is invalid; (*b*) the value of D employed in the free energy form is a statistically averaged value which is not the microscopic value that should be employed in the electrostatic theory. For the free energy this appears to be a minor matter, when water is the only solvent component. In the energy and entropy forms of the theory the temperature derivatives $\partial D/\partial T$ enter. It is conceivable that the averaged value of the derivatives may not be equal to the derivative of the average value of the integral property substituted in the equations, i.e.

$$\overline{\frac{\partial D}{\partial T}} \neq \frac{\partial \bar{D}}{\partial T}.$$

(*c*) Experimental errors which are not large enough to obscure the validity of the data in its free energy form become more prominent in the energy and entropy forms as a result of the differentiation over a small range of temperature.

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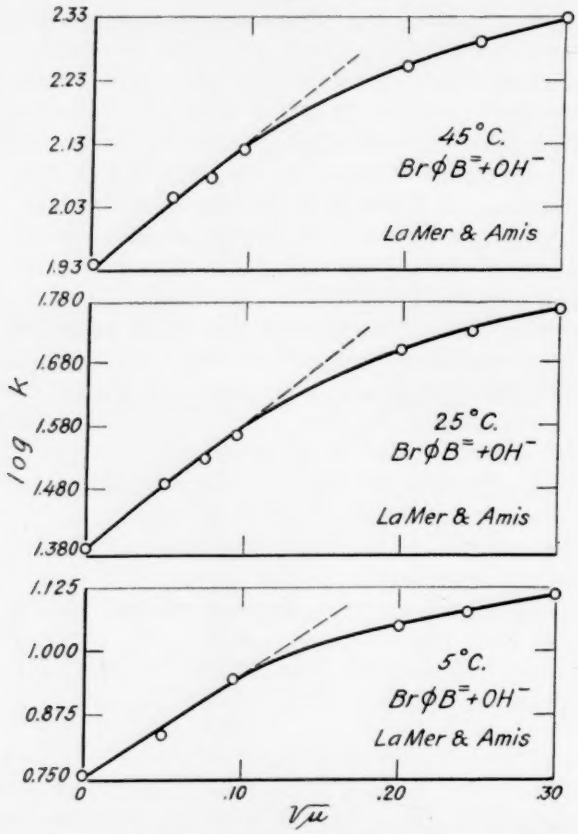
[35] Moelwyn-Hughes: *Proc. Roy. Soc.*, **155**, 308 (June, 1936).

[36] For some minor corrections see Moelwyn-Hughes, *Proc. Roy. Soc. A*, **157**, 667 (Dec., 1936). See footnote, p. 668.

Since an inspection of Panepinto and Kilpatrick's E values show many individual deviations of over 1000 calories, it becomes immediately apparent that their data are incompetent to determine the *concentration* dependence of E. Further-

FIG. 11.



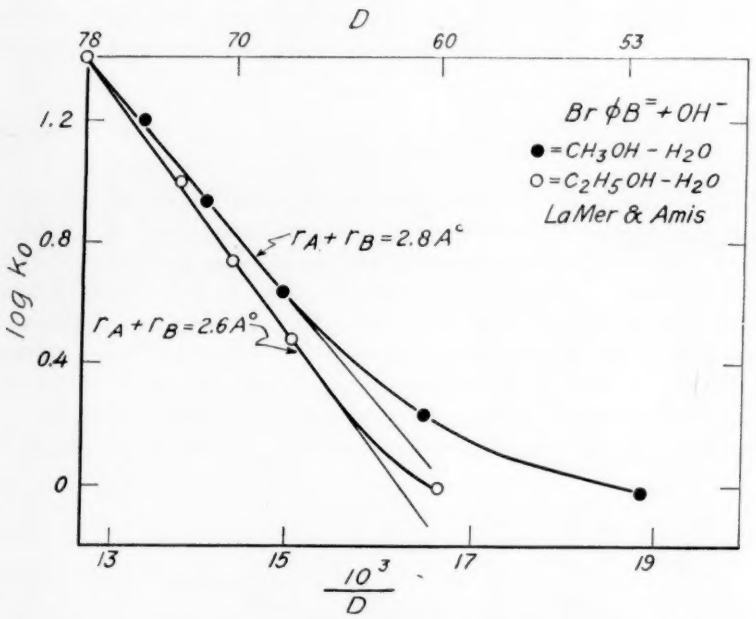
The concentration dependence of the log of velocity constants for the brom phenol blue hydroxyl ion reaction.

more, since the $r_A + r_B$ values calculated are surprisingly small—1.48, 1.61 and 1.68 Å for the iodo, bromo and chloro derivatives—Mr. Amis has undertaken under my direction a reinvestigation of the brom phenol blue reaction. By improving the colorimetric technique and by working over a

wider range of temperature 5, 25, 45° he has been able to reduce the experimental error considerably (see Fig. 11). His E values appear to be accurate to ± 50 calories.

In Fig. 12 log k at 25° C. is plotted against $1/D$ for ethyl and methyl alcohol additions. The values of $r_A + r_B$, equal to 2.6 Å and 2.8 Å from eq. (14), are entirely reasonable. The form of the curve is also very similar to that of Fig. 5.

FIG. 12.



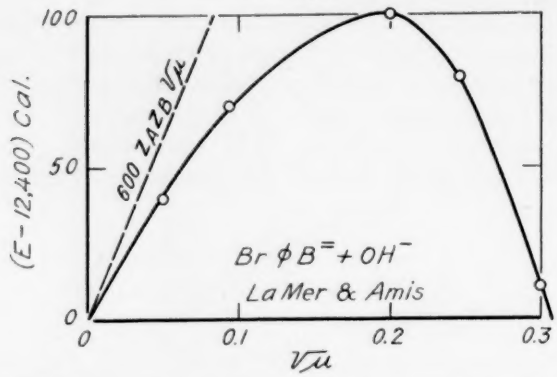
The dependence upon dielectric constant of the brom phenol blue hydroxyl ion reaction. The values of $r_A + r_B$ are calculated from equation 14.

The interaction a value best fitting the data in Fig. 11 is 5 Å at each temperature.

In Fig. 13 we give the energy of activation (E = 12,400 cal.) calculated for the interval 5–25° C.

The consistency of the experimental data, their approach to the limiting form of the heat of dilution equation as predicted by the Debye-Hückel theory, the maximum value at $\sqrt{\mu} = 0.2$, characteristic of so many heat of dilution curves at

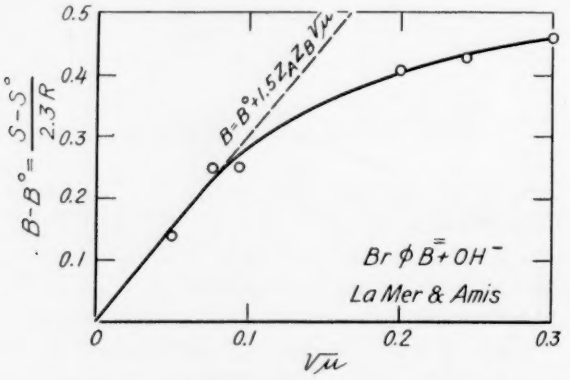
FIG. 13.



The energy of activation as a function of ionic strength for the brom phenol blue hydroxyl ion reaction. Computed from data at 5 and 25° C.

finite concentrations, strongly indicate that there are no serious discrepancies between these preliminary data of La Mer and Amis and the thermodynamic requirements of the electrostatic theory. The entropy contribution of electrostatic interaction is plotted in Fig. 14. Here the approach to the limiting law is all that could be expected. The data support the previous work [31] of this laboratory that the catalytic action of the primary salt effect is exercised primarily through an increase in the entropy of activation which is more than

FIG. 14.



The dependence upon ionic strength of the entropy of activation of the brom phenol blue hydroxyl ion reaction.

sufficient to counterbalance any rate depressing effect resulting from an increase in the energy of activation.

The heat capacity of activation appears to be -23 cal./deg./mol from our values of E_{5-25} and E_{25-45}, a value which is not inconsistent with the negative value of $\Delta C_p^* = [\bar{C}_{pX} - (\bar{C}_{pA} + \bar{C}_{pB})]$ to be expected from the available data on the partial molal heat capacities of ions as a function of their charge type. Since B is about 5 logarithmic units smaller than $\log Z$ or 7 units smaller than $\log kT/h$, this reaction belongs to the Case III of La Mer's classification of reactions as function of temperature.

An All Welded Multi-story Building.—G. D. FISH (*Civil Engineering*, Vol. 8, No. 4). The first completely welded building in New York City was recently constructed as two new wings for the main building of the State hospital in Brooklyn. The noiselessness of erection by welding was an undoubted advantage, in view of the fact that the new wings are immediately adjacent to a central tower housing some hundreds of mental patients and a numerous staff. This feature was not in any way responsible for the selection of welding because the choice was left to the contractor and was determined by cost alone. Steel design, not including connection details, was made the same for welding as for riveting, except that many beams in the lower stories were slightly lighter in section for welding. The two equal opposite hand wings were designed for nine stories, including the basement, but only six stories could be built within the present appropriation. The total steel in both wings amounted to 612 tons—approximately 60 tons less than the weight required by the design for riveting. Most of the saving was in the connections, especially in the wind bracing. The beams were not very heavy and the details for riveted wind bracing aggregated an unusually large tonnage in proportion to beam weight. In a building without wind bracing, riveted connections would probably not exceed 5 to 6 per cent. of the total weight, and welding could not save more than four fifths of that detail material. The building wings are about 350 ft. in combined length and 38 ft. wide. Most of the beams are connected to columns, but there are numerous trimmer and header beams at floor openings. The floor consists of two-way reinforced-concrete joists and hollow terra-cotta blocks. Outer walls are brick and terra-cotta. In conformity with prevailing standards, 18,000 lb. per sq. in. was used for direct stresses in rolled steel resulting from dead and live loads. For wind stresses alone, and for combinations of wind with other loads, unit stresses in welds and rolled steel were increased one third.

R. H. O.

THE COMPUTATION OF IONIZATION CONSTANTS AND LIMITING CONDUCTANCE VALUES FROM CONDUCTIVITY MEASUREMENTS.

BY

THEODORE SHEDLOVSKY, Ph.D.,

(From the Laboratories of The Rockefeller Institute for Medical Research.)

Before the interionic attraction theory for solutions was established it was customary to interpret the conductance of weak binary electrolytes on the basis of Arrhenius' theory and the Ostwald dilution law. The assumptions involved were, (1) that ionic mobilities remained constant with varying concentration, (2) that a thermodynamic equilibrium existed between unionized molecules and ions, (3) that the laws of ideal solutions were applicable, and (4) that the degree of ionization was given by the ratio of the equivalent conductance, Λ, divided by the value at infinite dilution, Λ_0.

The conductance equation based on these considerations is

$$\Lambda = \Lambda_0 - \frac{C\Lambda^2}{K\Lambda_0}, \qquad (1)$$

in which C is the concentration and K the ionization constant. Although we now know that the assumptions (1), (3), and (4) are not valid, equation (1) met with considerable success in the case of weak electrolytes due to a tendency for the errors to cancel.

For strong electrolytes, however, there was no adequate theory, but no lack of empirical equations. Kohlrausch, whose conductance measurements still remain among the most accurate and comprehensive, made the best guess with his "square root law." He found that in sufficiently dilute solutions his conductance determinations on most salts and strong acids followed the equation

$$\Lambda = \Lambda_0 - A\sqrt{C}, \qquad (2)$$

in which A is a constant.

The work of Debye and Hückel [1] and of Onsager [2] justified this formula on theoretical grounds. Onsager was able to compute accurately the constant $A = \alpha\Lambda_0 + \beta$, α and β being constants depending on the properties of the solvent and the temperature. However, his simple equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} \qquad (2a)$$

is, strictly speaking, a limiting formula. The linear relationship is valid up to a concentration of one or two thousandths normal (for 1–1 electrolytes in water), beyond which a curvature appears in the plots, corresponding to a progressive decrease in the slope, A, with rising concentration.

In solvents of high dielectric constant, such as water, strong electrolytes are completely ionized, an assumption inherent in Onsager's theory and well borne out by experimental results. On the other hand, in solvents of low dielectric constant no strong electrolytes exist. For such cases, Fuoss and Kraus [3] have interpreted conductance data in a manner analogous to equation (1) but corrected for interionic effects. They used Onsager's equation as a criterion for complete ionization for obtaining the degree of ionization, θ, and the Debye and Hückel activity coefficient equation for estimating deviations in the behavior of the ions from the laws of ideal solutions. Their problem was therefore to combine the following equations:

$$\theta = \frac{\Lambda}{\Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C\theta}}, \qquad (2b)$$

$$-\log f = a\sqrt{C\theta}, \qquad (3)$$

in which f is the activity coefficient and a is a constant depending on the dielectric constant and the temperature.

$$K = \frac{C\theta^2 f^2}{1 - \theta}. \qquad (4)$$

Equation (2b) is cubic in $\theta^{1/2}$, making the computations somewhat awkward. In a later publication,[4] Fuoss gave a useful

[1] Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).
[2] Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).
[3] Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).
[4] Fuoss, *ibid.*, **57**, 488 (1935).

table to simplify the computations of θ. He defined the functions

$$Z = \frac{(\alpha\Lambda_0 + \beta)}{\Lambda_0^{3/2}} \sqrt{C\Lambda},$$

and $F = f(Z)$, so that $\theta = \frac{\Lambda}{\Lambda_0 F}$. The resulting conductance equation, analogous to equation (1), is therefore

$$\frac{\Lambda}{F} = \Lambda_0 - \frac{1}{K\Lambda_0}\left(\frac{C\Lambda^2 f^2}{F^2}\right) \tag{5}$$

by combining (*2b*) and (4).

To determine Λ_0 and K from conductance data, it is necessary first to assume a tentative value for Λ_0. Values of $\frac{C\Lambda^2 f^2}{F^2}$ and $\frac{\Lambda}{F}$ are then computed and a plot of equation (5) is prepared. The intercept then gives a better value for Λ_0 and the process is repeated. It is rarely necessary to continue the approximation more than twice since the functions converge rapidly. The ionization constant K is obtained from the final plot by measuring the slope.

Returning to Onsager's equation (*2a*), I have observed that the decrease in the slope, A, of the plots Λ *vs.* $\sqrt{C}$ with rising concentration can be expressed quantitatively by the equation

$$\Lambda = \Lambda_0 - \frac{\Lambda}{\Lambda_0}(\alpha\Lambda_0 + \beta)\sqrt{C} \tag{6}$$

up to about $C = 0.01$. It will be recalled that Onsager's equation is a limiting law, so that (6) and (*2a*) are equivalent at very high dilutions. We may write (6) in the form

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{(\alpha\Lambda_0 + \beta)}{\Lambda_0^2}\sqrt{C}. \tag{6a}$$

Now this equation has certain practical advantages. It is in accord with the modern conductance theory and because of its validity over a greater ionic concentration range than (*2a*) (nearly tenfold) it is more suitable for purposes of extrapolation. Moreover, when used as a criterion for complete ionization, there results, for weak electrolytes, the simple

quadratic equation

$$\theta = \frac{\Lambda}{\Lambda_0} + \left(\frac{\alpha\Lambda_0 + \beta}{\Lambda_0^2}\right)\Lambda\sqrt{C\theta} \qquad (6b)$$

instead of the cubic equation (2*b*). This makes for considerable simplification in the Fuoss and Kraus treatment of conductance data on weak electrolytes, since no special tables are required.

Let us define, as Fuoss has done, a function

$$Z = \frac{(\alpha\Lambda_0 + \beta)}{\Lambda_0^{3/2}}\sqrt{C\Lambda}.$$

Then the solution of (6*b*) gives

$$\theta = \frac{\Lambda}{\Lambda_0}\left(\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2}\right)^2}\right)^2, \qquad (7)$$

which yields on expansion

$$\theta = \frac{\Lambda}{\Lambda_0}\left(1 + Z + \frac{Z^2}{2} + \cdots\right) \equiv \frac{\Lambda}{\Lambda_0}F. \qquad (7a)$$

For most practical purposes the last term can be neglected, so that $F = (1 + Z)$.

Combining this with (4) there results

$$\Lambda F = \Lambda_0 - \frac{F^2 f^2 \Lambda^2 C}{K\Lambda_0}, \qquad (8)$$

which is equivalent to (5), but holds for considerably higher ion concentrations, as stated above.

The question now arises as to what are the possible limitations in using the Fuoss and Kraus method, equation (5) or the suggested modification represented by equation (8), in interpreting and extrapolating conductance data on weak electrolytes. In media of low dielectric constant, where there are no strong electrolytes, there is no alternative. But in water we may, for example, obtain values of Λ_0 for weak acids, HA, by this method, and compare the results with values computed from the limiting conductances for the strong electrolytes, HCl, NaA, and NaCl.* When this comparison

* $\Lambda_{0(HA)} = \Lambda_{0(HCl)} + \Lambda_{0(NaA)} - \Lambda_{0(NaCl)}$.

is made, it is found that the two methods give essentially the same results provided the electrolyte is not too weak ($K \geqq 10^{-4}$).† If the electrolyte is much weaker ($K \leqq 10^{-5}$), the extrapolation to infinite dilution becomes longer and therefore less certain, since experimental difficulties set a limit to the dilutions accessible for accurate measurement. Therefore, in such cases, the alternative method, involving measurements on a strong acid and the two (strong) salts, should be used if possible. Here, the weakness of the acid is of no consequence, since perfectly reliable values for Λ_0 can be obtained from plots of $\frac{I}{\Lambda}$ *vs.* $\sqrt{C}$, equation (6*a*) being valid for the completely ionized electrolytes involved. However, equation (5) or (8) can be used for accurately computing the ionization constant K from the conductance of a weak electrolyte if Λ_0 is well known. Or, *vice versa*, if K is known, Λ_0 can be computed.

† Dr. Donald Belcher has carried out such a comparison with measurements, soon to be published, on organic acids.

Scientific Body Measurements Needed.—B. S. YANE. (*Industrial Standardization*, Vol. 9, No. 4.) Probably one of the best known of the wasteful and archaic practices which can still be found at times despite our scientific progress in industry is the way in which ready-to-wear clothing is marked for size. In a study of returned goods made by Ada Lillian Bush of the U. S. Department of Commerce, women's and children's clothing accounted for over 40 per cent. of the merchandise returned. For all merchandise, the reason for return given most frequently was wrong size and in many cases the customer feels that the producer is responsible for and could correct the situation. The majority of consumers stressed the lack of uniformity in measurements and proportions of similar products produced by different manufacturers. The measurement of the United States Army soldiers at the close of the World War represents about the only "scientifically acceptable" study of clothing sizes which has been made. Unfortunately, these measurements are not adaptable to the construction of civilian clothing. At the present time definite plans have been formulated for a scientific study of body measurements to be conducted under the supervision of Ruth O'Brien, of the U. S. Bureau of Home Economics. The project calls for the measurement of 100,000 children of both sexes at 11 age levels, 4 through 14, in eight selected regions of the United States. With the idea of using this study to establish an "American Standard" for sizes of children's garments, a sectional committee has been set up by the American Standards Association. A staff of statisticians and trained anthropometrists is supervising the field work of the study. If the results of the study prove that a system of scientific body measurements provides a more practical and usable basis for children's clothing patterns and sizes than present methods, there will then be good reason to expect that the same technique when applied to the solution of the sizing problems in adults' ready-made clothing will be successful.

R. H. O.

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

SERVICEABILITY OF SHOES CONSTRUCTED IN DIFFERENT WAYS.

The increasing interest in standards for footwear is shown by the number of requests which the Bureau receives from organizations and individuals for information about the methods of shoe construction in common use. The comparative merits of shoes of different constructions, from the point of view of service, and the feasibility of marking shoes as to the type of construction for the benefit of the consumer, are questions raised frequently. Circular C419 discusses these questions.

An analysis of the figures for annual shoe production is included, from which an idea may be obtained concerning the importance of each main class of construction in relation to the total number of shoes manufactured. This gives a general picture of what the consumer is buying.

The terms generally used to denote types of construction are: (1) Welt, (2) McKay, (3) Littleway, (4) Turn, (5) Stitchdown, (6) Nailed, (7) Cemented, and (8) Moccasin. It is shown, however, that these names by no means convey the necessary information regarding the various types of construction used. More than forty individual constructions are described and classified under the eight headings listed above. Individual constructions in a main group vary among themselves to such a degree that a group name is not indicative of the true construction used. The value to the consumer of marking shoes is discussed and it is pointed out that such marking is of doubtful value because of the many grades of shoes which can be made by the same method of construction.

Performance tests of ladies' leather shoes on a laboratory endurance machine have shown that shoes of four different constructions, made of the same quality of materials and the same standards of workmanship, will stand up equally well

* Communicated by the Director.

on the machine while making 1,000,000 steps under normal conditions of load and flexure.

The subject matter will doubtless be of interest to consumers, to manufacturers, and retailers of shoes, and to students of home economics. Copies of this Circular are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 10 cents each.

APPLICATION OF THERMODYNAMICS TO THE CHEMISTRY OF RUBBER.

Measurements of the basic thermodynamic constants of rubber which have been made at the Bureau during the past few years are summarized and correlated in a paper on "Application of Thermodynamics to the Chemistry of Rubber." This paper will be presented by Dr. Norman Bekkedahl at the World Conference on Rubber Technology which is to be held in London in May, 1938.

The introductory part of this paper deals with the general methods whereby the change in free energy of a chemical reaction may be employed in the prediction of the direction and the driving force of that reaction under various conditions. This thermodynamic function is applied in the paper to the reaction

$$\text{isoprene} \rightleftharpoons \text{rubber}.$$

The change in free energy (often called the thermodynamic potential) of the above reaction is obtained as the difference between the free energies of formation of the rubber and of the isoprene from their elements, carbon and hydrogen. These free energies of formation are calculated from measurements of the entropies and heats of combustion of the rubber and the isoprene.

The entropy and the heat of combustion of rubber have been reported in *J. Research N.B.S.*, **15**, 503 (1935) (RP844) and **13**, 357 (1934) (RP713), respectively; similar data on isoprene are given in *J. Research N.B.S.*, **19**, 551 (1937) (RP1044) and **20** (May 1938) (RP1093), respectively. A general discussion of the relation between the different amorphous and crystalline forms of rubber have been given in *J. Research N.B.S.*, **13**, 411 (1934) (RP717).

At 298.2° K. (25° C.) the difference in free energies of the isoprene and the rubber is such as to favor strongly the formation of rubber from isoprene. With increasing temperature, however, this difference becomes progressively less, and at about 800° K. (527° C.) at atmospheric pressure the balance shifts, and above this temperature the reaction proceeds in the direction favoring the formation of isoprene from rubber.

HEAT OF COMBUSTION OF ISOPRENE.

A paper by Ralph S. Jessup (RP1093) in the *Journal of Research* for May, reports part of an investigation undertaken to provide data for a study of the thermodynamics of reactions involving rubber and related substances. In previous papers data have been reported on the heat of combustion of rubber, on the entropy and free energy of formation of rubber, and on the entropy of isoprene. An accurate value for the heat of combustion of isoprene was required for use with the entropy of formation in calculating the free energy of formation of this substance. The importance of data on the properties of isoprene may be seen from the following facts: Isoprene is closely related to rubber in its chemical composition, having the same empirical formula, C_5H_8; it is one of the two principal products of the destructive distillation of rubber; it can be polymerized to form a product similar in its properties to natural rubber; and it is thought to be the substance from which rubber is formed in plants, and to play an important role in the growth of plant cells.

The measurements of heat of combustion of the liquid isoprene were made by means of a bomb calorimeter which was calibrated with N.B.S. standard sample benzoic acid. To prevent evaporation of the liquid in the bomb, the samples were inclosed in thin-walled glass bulbs which were flattened on opposite sides and filled completely with the liquid. The yielding of the flexible flat side of the bulbs under pressure of the oxygen in the bomb was sufficient to transfer the support of the pressure to the inclosed liquid, and the bulbs did not break until the electric fuse used to ignite the samples was fired. No combustible material other than the iron wire of

the electric fuse was required to ignite the samples. The amount of isoprene burned in each experiment was determined from the mass of CO_2 formed in combustion, thus eliminating errors from inert impurities in the sample and reducing those arising from uncertainty in the atomic weight of carbon.

Seven experiments to determine the heat of combustion of liquid isoprene at 25° C., under a constant pressure of 1 atmosphere gave the value 3156.9 ± 1.6 international kilojoules per mole, when the products of combustion are liquid water and gaseous CO_2. This is higher by about 2.5 per cent. than the value previously obtained for the heat of combustion of rubber per C_5H_8 unit. The corresponding value for the heat of combustion of gaseous isoprene is calculated to be 3182.8 ± 1.7 international joules per mole.

BOILING POINTS OF BENZENE, ETHYLENE CHLORIDE, n-HEPTANE AND 2,2,4-TRIMETHYLPENTANE.

By the comparative ebulliometric method, using water as the reference standard and ebulliometers of the Swietoslawski type, data were obtained from which were developed equations expressing the relation between temperature and vapor pressure from 660 to 860 mm. for benzene, ethylene chloride, *n*-heptane, and for 2, 2, 4-trimethylpentane (isooctane).

In RP1097, by Edgar Reynolds Smith and Harry Matheson, which will be published in the May number of the *Journal of Research*, these equations are given, and the use of these substances as reference standards for boiling point measurements is discussed. Equations for the relative volatilities of the 2 pairs, benzene-ethylene chloride and *n*-heptane, 2, 2, 4-trimethylpentane are presented. The data show that Duhring's rule and the corresponding reciprocal temperature relationship hold accurately over a limited range of pressures, even for substances of different types.

COOLING RATE OF IRON-CARBON ALLOYS AND CARBON STEELS.

The depth to which steel will harden is influenced by its composition and grain size at the time of quenching. In the

Bureau's Division of Metallurgy, Thomas G. Digges has been making some experiments to determine the role that carbon plays in controlling the hardenability of high-purity iron-carbon alloys and plain carbon steels. To accomplish this a series of high-purity iron-carbon alloys and two series of plain carbon steels were prepared, in which the chemical composition of each series was kept constant except for the amounts of carbon present. The preparation of these alloys and steels and their hardening properties for various conditions are discussed in RP1092 in the May *Journal of Research.*

Analyses made on specimens of the iron-carbon alloys showed that they contained neglibible amounts of impurities, the value for all those determined being only about 0.03 per cent. by weight.

The critical cooling rate, that is, the slowest cooling rate for which the steel will be fully hardened, was determined under controlled conditions for both the high-purity iron-carbon alloys and carbon steels. The critical cooling rate was then used as an index of the hardenability of these alloys and steels.

It has been usually believed that plain carbon steels containing about 0.80 to 0.90 per cent. of carbon have slower critical cooling rates, i.e., are deeper hardening, than similar carbon steels containing either lower or higher amounts of carbon.

In the present experiments, it was shown that the carbon steel, containing about 0.80 per cent. of carbon, was deeper hardening than the higher carbon steels only for the conditions where the hardenability of the steels was influenced by factors such as variations in grain size or when all carbon was not in solution at the time of quenching.

In the experiments where average grain size was constant and all carbon was in solution at the time of quenching, it was shown that the critical cooling rate decreased continuously as the carbon content increased for the iron-carbon alloys and also for the steels. In other words, the iron-carbon alloy containing the highest amount of carbon (1.21 per cent.) had the greatest depth of hardening of this entire series of alloys, and likewise the carbon steel containing the highest amount of carbon had the greatest depth of hardening

of that entire series. However, to utilize the full hardening power of the alloys and steels, it was necessary to heat them to temperatures sufficiently high to insure the complete solution of the carbon.

Comparison of the hardenability of the high-purity iron-carbon alloys and plain carbon steels shows that the former were comparatively shallow hardening. This difference in hardenability was due to the higher manganese content of the steels.

An important feature brought out in these experiments, therefore, is the influence of the dissolved carbon content of the alloys and steels at the time of quenching on their hardenability.

THE FRANKLIN INSTITUTE.

MEDAL DAY MEETING.

The annual Medal Day Meeting, which is usually held on the third Wednesday of May, was this year held on Friday, May 20, as a part of the ceremonies of the dedication of the Benjamin Franklin Memorial. The meeting was called to order at 8:30 o'clock P.M. by the President, Mr. Philip C. Staples.

All the awards recommended by the Committee on Science and the Arts were then made.

	Sponsor
Presentation of Longstreth Medals to CLARENCE W. BALKE, Ph.D., Fansteel Metallurgical Corporation, Chicago, Illinois.	Mr. W. H. Fulweiler
FREDERICK HELLWEG, CAPTAIN, U. S. N. Ret., and PAUL SOLLENBERGER, United States Naval Observatory, Washington, D. C.	Mr. James Stokley
FREDERICK C. LANGENBERG, Sc.D. (Awarded Posthumously) and NORMAN F. S. RUSSELL, President, United States Pipe and Foundry Company, Burlington, New Jersey.	Mr. Coleman Sellers, 3rd
CARL ZEISS, Incorporated, Jena, Germany, and DYCKERHOFF AND WIDMANN AKTIEN GESELLSCHAFT Berlin, Germany.	Mr. W. C. Cushing
Presentation of Clark Medal to ROBERT BRINTON HARPER, The Peoples Gas Light and Coke Company, Chicago, Illinois.	Mr. J. B. Klumpp
Presentation of Henderson Medal to CLYDE C. FARMER, Westinghouse Air Brake Company, Pittsburgh, Pennsylvania.	Mr. C. D. Galloway

Presentation of Levy Medals to
STEWART S. KURTZ, JR., Mr. L. F. Levy
Sun Oil Company,
Marcus Hook, Pennsylvania,
and
ALGER L. WARD,
United Gas Improvement Company,
Philadelphia, Pennsylvania.

Presentation of Potts Medal to
LARS O. GRONDAHL, Ph.D., Mr. Edward W. Smith
Union Switch and Signal Company,
Swissvale, Pennsylvania.

Presentation of Cresson Medal to
EDWIN H. LAND, Dr. C. B. Bazzoni
The Land-Wheelwright Laboratories, Incorporated,
Boston, Massachusetts.

Presentation of the Franklin Medal and
Certificate of Honorary Membership to
WILLIAM FREDERICK DURAND, Ph.D., LL.D., Dr. H. J. Creighton
Stanford University,
California.

Presentation of the Franklin Medal and
Certificate of Honorary Membership to
CHARLES AUGUST KRAUS, Ph.D., Dr. H. J. Creighton
Brown University,
Providence, Rhode Island.

Following the presentation of awards, Dr. Thomas S. Gates, President of the University of Pennsylvania, took the chair and conferred the degree of Doctor of Science upon

GEORGE DAVID BIRKHOFF
ARTHUR LOUIS DAY
GILBERT NEWTON LEWIS
THOMAS HUNT MORGAN
LOUIS MARTIN

who participated in the dedicatory ceremonies.*

Adjourned.

HENRY BUTLER ALLEN,
Secretary.

* A detailed account of the ceremonies will appear later.

CERTIFIED FINANCIAL STATEMENTS

as at December 31, 1937.

April 19, 1938.

To the Board of Managers of
The Franklin Institute,
Philadelphia.

We have made an examination of the balance sheet of THE FRANKLIN INSTITUTE as at December 31, 1937, and of the statements of income and expenses and general fund for the fifteen months ended that date. In connection therewith, we examined or tested accounting records of the Institute and other supporting evidence, and obtained information and explanations from officers and employees of the Institute; we also made a general review of the accounting methods, of the income accounts as recorded, and of the operating and fund accounts for the period, but we did not make a detailed audit of the transactions. The buildings and equipment and investments are stated at cost or appraised values at dates of acquisition, and do not purport to represent present day values.

Subject to the foregoing, the annexed financial statements, in our opinion, fairly present, in accordance with accepted principles of accounting consistently maintained by the Institute during the period under review, the financial position of The Franklin Institute at December 31, 1937, and the results of its operations for the fifteen months ended that date, after excluding the accounts of The Bartol Research Foundation of The Franklin Institute on which separate reports were submitted for the year ended September 30, 1937, and of The Biochemical Research Foundation of The Franklin Institute, on which separate reports were submitted for the year ended August 31, 1937.

(Signed) LYBRAND, ROSS BROS. & MONTGOMERY.

THE FRANKLIN INSTITUTE.

BALANCE SHEET, DECEMBER 31, 1937.

Assets.

Cash in banks and on hand (not including cash in endowment trust funds)		$34,670.31
Accounts receivable for memberships, subscriptions, etc.		12,774.62
Materials and supplies, at cost		6,199.32
Buildings and equipment, at cost, not including exhibits loaned and donated		4,039,236.97
Deferred expenses		7,195.55
		$4,100,076.77
Endowment fund investments, cash, etc.:		
Investments, at cost or appraised values at the dates of acquisition	$2,371,144.02	
Deposit in closed bank, less reserve	85,000.00	
Cash:		
Uninvested principal	8,772.14	
Unexpended income	7,336.41	
		2,472,252.57
		$6,572,329.34

Liabilities.

Accounts payable		$19,936.64
Amounts received for life memberships not transferred to General Endowment Fund		500.00
Deferred income from dues, etc.		41,095.95
Contributed funds used for buildings, equipment, etc., as annexed		3,902,492.98
Stock outstanding:		
First class	$12,940.00	
Second class	70.00	
		13,010.00
General Fund account, as annexed		123,041.20
Endowment funds:		
Principal, as annexed	2,464,916.16	
Unexpended income	7,336.41	
		2,472,252.57
		$6,572,329.34

GENERAL FUND ACCOUNT

for the fifteen months ended December 31, 1937.

Balance, October 1, 1936		$169,783.49
Add:		
Amount withdrawn from Museum Reserve Fund Principal for capital and operating expenses	$53,000.00	
First Class Stock surrendered and cancelled	100.00	
Equipment previously charged to expense, restored to books as an asset (air show)	150.00	
		53,250.00
		$223,033.49
Deduct:		
Difference between book value and net amount received for premises Nos. 13–15–17 South Seventh Street, Philadelphia, Pa.	$32,871.70	
Deficit for the period, as annexed	67,120.59	
		99,992.29
Balance, December 31, 1937		$123,041.20

INCOME AND EXPENSE ACCOUNT

for the fifteen months ended December 31, 1937.

Income.

Dues, initiation fees, etc.		$26,649.48
Less dues uncollected, prior years		750.50
		25,898.98
Admissions to museum and planetarium, sale of guide books, etc.		94,529.39
Subscriptions to publications and advertising		8,999.39
Donations		18,710.53
Administrative charges for services rendered The Bartol Research Foundation and The Biochemical Research Foundation		13,500.01
Miscellaneous income, net of expenses incident thereto		2,372.35
		164,010.65
Income from trust fund investments, etc.		143,850.51
		$307,861.16

Expenses.

	Salaries and Wages.	Other.	
Building operation and maintenance	$45,674.01	$36,100.13	
Library	17,695.53	6,792.90	
Meetings	—	2,893.31	
Office and general	59,070.04	17,024.10	
Machine shop	757.55	457.16	
Museum	111,615.37	47,731.72	
Publications	—	16,432.01	
Science and the Arts	4,454.16	461.91	
Traveling expense	—	1,403.19	
Annuities	3,906.27	—	
Interest and discount	—	2,442.39	
Membership badges and certificates	—	70.00	
	$243,172.93	$131,808.82	
			$374,981.75
Deficit for the fifteen months ended Dec. 31, 1937			$ 67,120.59

SUMMARY OF CHANGES IN ENDOWMENT FUNDS

for the fifteen months ended December 31, 1937.

Balances October 1, 1936		$2,573,998.44
Add:		
Profit on sale or call of investments	$64,123.95*	
Amounts received for life memberships	1,200.00	
New gift and bequest	20,000.00	
Miscellaneous	23.36	
		85,347.31
		$2,659,345.75
Deduct:		
Losses on sale of investments	54,226.85	
Amount withdrawn from the Museum Reserve Fund for capital and operating expenditures, credited to General Fund Account	53,000.00	
Amount received as a distribution from principal of the John G. Meigs Bequest, credited to John G. Meigs Memorial Fund (income account)	11,202.74	
Repayment of loan from Benjamin Franklin Memorial, Inc.	76,000.00	
		194,429.59
Balances December 31, 1937		$2,464,916.16

* Includes $1,913.81 profit on transfer of General Endowment Fund investments at market value, to Museum Reserve Fund investments.

CONTRIBUTED FUNDS RECEIVED FROM
BENJAMIN FRANKLIN MEMORIAL, INC.,

for the fifteen months ended December 31, 1937.

Balance October 1, 1936		$3,818,494.56
Add:		
Pledges collected	$ 7,998.42	
Loan repaid by The Franklin Institute	76,000.00	
		83,998.42
Balance December 31, 1937		$3,902,492.98

THE BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

CERTIFIED FINANCIAL STATEMENTS

as at September 30, 1937.

December 22, 1937.

To the Board of Directors of
The Franklin Institute,
Philadelphia.

We have made an examination of the balance sheet of THE BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE as at September 30, 1937, and of the statement of income and expenses for the year ended that date. In connection therewith, we examined or tested accounting records of the Foundation and other supporting evidence and obtained information and explanations from officers and employees of The Franklin Institute; we also made a general review of the operating and fund accounts for the period, but we did not make a detailed audit of the transactions. The building, which is located on the property of Swarthmore College, and the equipment are stated at cost and the investments at cost or appraisal values at dates of acquisition and do not purport to represent present day values. The cost of books and scientific literature is charged to expense.

Subject to the foregoing, the accompanying balance sheet and related statement of income and expenses, in our opinion fairly present, in accordance with accepted principles of ac-

counting consistently maintained by the Foundation during the year under review, its financial position at September 30, 1937, and the results of its operations for the year ended that date.

(Signed) LYBRAND, ROSS BROS. & MONTGOMERY.

THE BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

BALANCE SHEET, SEPTEMBER 30, 1937.

Assets.

Cash:			
In bank and on hand, general fund		$3,366.23	
Unexpended income:			
Henry W. Bartol Bequest	$15,336.94		
Investment of unexpended income fund	7,965.63	23,302.57	
			$26,668.80
Investments of unexpended income fund, at cost			202,610.10
Building and equipment, at cost:			
Laboratory building		226,591.05	
Furniture and fixtures		14,874.93	
Equipment:			
Laboratory	82,170.40		
Less allowance for depreciation	15,523.93	66,646.47	
Machine shop	16,831.75		
Less allowance for depreciation	2,168.51	14,663.24	
Building		375.00	
Office		3,013.47	
Library		1,057.65	
			327,221.81
			$556,500.71

Investments (at cost or appraised values at dates of acquisition) and cash of principal of trust funds:

	Investments.	Cash.	
Henry W. Bartol Bequest	$1,332,241.59	$5,093.70	
Pension fund	70,385.23	2,658.81	
	$1,402,626.82	$7,752.51	
			1,410,379.33
			$1,966,880.04

Collateral Trusts.

Cash:			
Uninvested principal	$15,390.65		
Undistributed income	2,773.10	$18,163.75	
Investments:			
Helene Bonar Bartol Trust	305,669.21		
Lucy Cheyney Farr Trust	148,844.55		
Katherine de Monclos Trust	152,571.13	607,084.89	
			625,248.64
			$2,592,128.68

Liabilities.

Accounts payable		$2,226.02
General Fund account:		
Balance, October 1, 1936	$546,771.22	
Excess of income over expenses for the year ended September 30, 1937, as annexed	7,503.47	
		554,274.69
		$556,500.71
Endowment Funds:		
Henry W. Bartol Bequest	1,337,335.29	
Pension fund	73,044.04	
		1,410,379.33
		$1,966,880.04

Collateral Trusts.

Principal:			
Helene Bonar Bartol Trust	$311,117.91		
Lucy Cheyney Farr Trust	155,748.55		
Katherine de Monclos Trust	155,609.08		
		622,475.54	
Undistributed income		2,773.10	
			625,248.64
			$2,592,128.68

INCOME AND EXPENSE ACCOUNT

for the year ended September 30, 1937.

Income.

Income received from investments	$63,221.16
Other income:	
Profit, net of losses, on sale of income investments	4,378.30
	$67,599.46

Expenses.

	Salaries and Wages.	Other.	
Building operation and maintenance	$1,071.99	$2,741.57	
Library	—	858.08	
Administrative and general	15,100.00	2,117.76	
Laboratory and machine shop	23,904.36	3,723.53*	
Publications, reprints	—	359.70	
Traveling expense	—	95.20	
Administrative charge, The Franklin Institute	—	6,000.00	
Investment counsel charge	—	4,123.80	
	$40,076.35	$20,019.64	
			60,095.99
Excess of income over expenses for the year, transferred to General Fund Account			$ 7,503.47

* Includes provision of $949.20 for depreciation of laboratory equipment.

THE BIOCHEMICAL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

CERTIFIED FINANCIAL STATEMENTS

as at August 31, 1937.

December 22, 1937.

To the Board of Managers of
The Franklin Institute,
Philadelphia.

We have made an examination of the balance sheet of THE BIOCHEMICAL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE as at August 31, 1937, and of the statement of expenses and income for the year ended that date. In connection therewith, we examined or tested the accounting records of the Foundation and other supporting evidence and obtained information and explanations from officers and employees of The Franklin Institute; we also made a general review of the accounting methods and of the operating and fund accounts for the period, but we did not make a detailed audit of the transactions. The research apparatus and other

equipment are stated at their appraised values on July 1, 1935, with additions since that date at cost; the investments are stated at appraised values at dates of acquisition.

Subject to the foregoing, the accompanying balance sheet and the related statement of expenses and income, in our opinion, fairly present, in accordance with accepted principles of accounting consistently maintained by the Foundation during the period under review, its financial position at August 31, 1937, and the results of its operations for the year ended that date.

(Signed) LYBRAND, ROSS BROS. & MONTGOMERY.

THE BIOCHEMICAL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

BALANCE SHEET, AUGUST 31, 1937.

Assets.

Cash:		
In general checking account and on hand	$8,201.71	
Unexpended cash of funds available for current operations:		
Biochemical Research Foundation $21,696.31		
Emma M. Schaible Bequest 1,042.69	22,739.00	
Unexpended cash of funds available for bonuses to employees (see contra)	8,054.05	
Unexpended cash of fund available for special clinical work (see contra)	1,000.00	
		$39,994.76
Investments, at appraised values at dates of acquisition:		
Biochemical Research Foundation	183,500.00	
Emma M. Schaible Bequest	1,760.50	
		185,260.50
Equipment, at appraised value July 1, 1935, with subsequent additions at cost:		
Research apparatus and equipment	$134,545.87	
Improvements to leased equipment	10,783.51	
Cyclotron experiment	17,984.90	
Library books	2,663.07	
		165,977.35
200 shares Hendry-Connell Research Foundation, Ltd., par value $100, at nominal value		2.00
Deferred charge, amount due under agreement (see contra)		25,000.00
		$416,234.61

Liabilities.

Accounts payable	$1,069.91
Amount due Hendry-Connell Research Foundation, Ltd., pledged for the year ending August 31, 1938, under terms of agreement dated December 6, 1935 (see contra)	25,000.00
	26,069.91
Unexpended income of funds available for bonuses to employees (see contra)	8,054.05
Unexpended balance of special gift for clinical work in the distribution and application of ensol (see contra)	1,000.00
General Fund account, as annexed	381,110.65
	$416,234.61

STATEMENT OF EXPENSES AND INCOME

for the year ended August 31, 1937.

Expenses.

	Salaries and Wages.	Other.	
Building operation and maintenance	—	$11,307.71	
Administrative and general	$31,440.16	3,352.84	
Laboratory	90,338.66	13,538.38	
Publications and printing	—	1,159.88	
Special publications expense	—	2,600.00	
Dues and subscriptions	—	1,112.56	
Traveling and entertainment	—	2,440.21	
Administrative charge, The Franklin Institute	—	4,999.97	
Miscellaneous	—	587.51	
	$121,778.82	$41,099.06	$162,877.88
Advance to the Hendry-Connell Research Foundation, Ltd., under agreement dated December 6, 1935			25,000.00
			$187,877.88

Income.

Donation	$10.00	
Income received from investments	213.40	
Other income:		
Profit on sale of investments	28,857.50	
		29,080.90
Excess of expenses over income for the period, transferred to General Fund account		$158,796.98

GENERAL FUND ACCOUNT

for the year ended August 31, 1937.

Balance, September 1, 1936		$432,489.44
Add:		
Appraised value of 50 shares Christiana Securities Company common stock, received as donation	$91,750.00	
Amount previously designated for special purposes, now available for general purposes	15,568.19	
Contribution received from Mrs. John L. Randall	100.00	
		107,418.19
		$539,907.63
Less excess of expenses over income available for purposes of the Foundation, for the year ended August 31, 1937, as annexed		158,796.98
Balance, August 31, 1937		$381,110.65

LIBRARY NOTES.

The Committee on Library desires to add to the collections of the Institute any technical writings of members who have had occasion to publish such material.

Literary contributions from author-members will be gratefully acknowledged, properly inscribed and noted in the Journal of the Institute.

Photostat Service. Photostat prints of any material in the collections can be supplied on request. Orders received in the morning are filled the same day. The average cost for a print $8\frac{1}{2} \times 11$ inches is thirty-five cents.

The library and reading room are open daily from nine o'clock A.M. until five o'clock P.M. Saturdays until 12 o'clock noon. 719 readers made use of the facilities during the twenty-five days of April.

RECENT ADDITIONS.

Agriculture and Forestry.

BOYCE, JOHN SHAW. Forest Pathology. First Edition. 1938. American Forestry Series.

Astronomy.

GUNTHER, ROBERT T. The Astrolabes of the World. Volume I: The Eastern Astrolabes; Volume II: The Western Astrolabes. 1932.

Aviation.

Aircraft Year Book for 1938.

HADDON, J. D. A Simple Study of Flight. 1937.

JONES, H. A. The War in the Air. Volume VI and Appendices. 1937.

LEYSON, BURR. American Wings: Modern Aviation for Everyone. 1938.

MACKEY, JOSEPH C. Skywriting and Skywriting Equipment. 1937.

NELSON, WILLIAM. Seaplane Design. First Edition. 1934.
NILES, ALFRED S., AND JOSEPH S. NEWELL. Airplane Structures. Volume I. Second Edition. 1938.

Biography.

BERDROW, WILHELM. Alfred Krupp und sein Geschlecht. 1937.

Biology and Biochemistry.

BALDWIN, ERNEST. An Introduction to Comparative Biochemistry. 1937.
BLOCK, RICHARD J. The Determination of the Amino Acids. 1938.
GROBER, J. Die Akklimatisation. 1936.
HARVEY, RODNEY BEECHER. An Annotated Bibliography of the Low Temperature Relations of Plants. Revised Edition. 1936.
HOLMES, ERIC. The Metabolism of Living Tissues. 1937.
JENSEN, P. BOYSEN. Growth Hormones in Plants. Translated and Revised by George S. Avery, Jr. and Paul R. Burkholder. First Edition. 1936.
STEPP, W., J. KÜHNAU AND H. SCHROEDER. Die Vitamine und ihre klinischen Anwendung. Dritte unveränderte Auflage. 1938.
WEAVER, JOHN E., AND FREDERIC E. CLEMENTS. Plant Ecology. Second Edition. 1938.

Chemistry and Chemical Technology.

American Institute of Chemical Engineers. Transactions 1937. Volume 33. 1938.
ANDRADE, E. N. DA C. The New Chemistry. 1936.
BERNHAUER, KONRAD. Gärungschemisches Praktikum. 1936.
BÖMER, A., A. JUCKENACK, AND J. TILLMANS. Handbuch der Lebensmittelchemie. Siebenter Band: Alkoholische Genussmittel. 1938.
BÖTTGER, WILHELM, ED. Newer Methods of Volumetric Chemical Analysis. Translated by Ralph E. Oesper. 1938.
BRANDENBURGER, KURT. Herstellung und Verarbeitung von Kunstharzpressmassen. Zweite Auflage. 1938.
FINDLAY, ALEXANDER. A Hundred Years of Chemistry. 1937.
FRANKENBURGER, W. Katalytische Umsetzungen in homogenen und enzymatischen Systemen. 1937.
FRICKE, R., AND G. E. HÜTTIG. Hydroxyde und Oxydhydrate. 1937.
GRANT, JULIUS. Books & Documents: Dating, Permanence and Preservation. 1937.
JONES, ARTHUR. Cellulose Lacquers, Finishes and Cements. 1937.
MCGRATH, RAYMOND, AND A. C. FROST. Glass in Architecture and Decoration. 1937.
MARCHIONNA, FREDERICK. Latex and Rubber Derivatives and their Industrial Applications. Volumes 2–3. 1937.
Society of Chemical Industry. Reports on the Progress of Applied Chemistry. Volume 22. 1937.
STILLWELL, CHARLES W. Crystal Chemistry. 1938.

Directories.

Dyer, Textile Printer, Bleacher and Finisher. The Dyers' Index. 1937.
Index Generalis. 1938.

Electricity and Electrical Engineering.

MOELLER, FRIEDRICH. Versuche zur elektrischen Resonanz mit hochfrequenten und niederfrequenten Wechselströmen. 1937.

SIEMENS-WERKEN. Wissenschaftliche Veröffentlichungen XVII Band, Erstes Heft. 1938.

Société Française des Électriciens. Commémoration du Cinquantenaire des Premières Réalisations de Transmission d'Énergie par l'Électricité. 1935.

South Kensington Science Museum. Television. Edited by G. R. M. Garratt Assisted by G. Parr. 1937.

VILBIG, FRITZ. Lehrbuch der Hochfrequenztechnik. 1937.

Engineering.

MORLEY, S. GRISWOLD. The Covered Bridges of California. 1938.

Founding.

Institute of British Foundrymen. Proceedings. Volume 30. 1936–1937.

Geography and Travel.

BELL, ALAN. The Said Noble River. 1937.

Geology and Geophysics.

ARLDT, THEODOR. Die Entwicklung der Kontinente und ihrer Lebewelt. Zweite, vollständig neubearbeitete und erweiterte Auflage. Erster Teil. 1936.

Great Britain. Geological Survey and Museum. The First Hundred Years of the Geological Survey of Great Britain by Sir John Smith Flett. 1937.

Great Britain. Imperial Institute. The Mineral Industry of the British Empire and Foreign Countries. Statistical Summary (Production, Imports and Exports) 1934–1936. 1937.

Great Britain. Imperial Institute. Mineral Resources Department. Asbestos (Second Edition) by G. E. Howling. 1937.

Great Britain. Imperial Institute. Mineral Resources Department. Barium Minerals (Second Edition) by J. Simpson. 1937.

SELIGMAN, G. Snow Structure and Ski Fields. 1936.

South Kensington. Science Museum. Applied Geophysics. 1936.

Hygiene and Physiology.

EULENBURG-WIENER, RENÉE VON. Fearfully and Wonderfully Made. 1938.

Mathematics.

British Association for the Advancement of Science. Mathematical Tables. Volumes 1–6. 1931–1937.

DOETSCH, GUSTAV. Theorie und Anwendung der Laplace-Transformation. 1937.

Metallurgy.

BITTER, FRANCIS. Introduction to Ferromagnetism. First Edition. 1937.

BURKHARDT, ARTHUR. Zink und seine Legierungen. 1937.

Military Science.

OMAN, SIR CHARLES. A History of the Art of War in the Sixteenth Century. 1937.

Naval Architecture.

Brassey's Naval Annual. 1938.
Society for Nautical Research. Lists of Men-of-War. Pts. 1–4. 1935–1938.
State Street Trust Company. Some Ships of the Clipper Ship Era. 1913.
State Street Trust Company. Whale Fishery of New England. 1915.

Pharmacy.

BENTLEY, ARTHUR OWEN. A Text-Book of Pharmaceutics. Fourth Edition. 1937.

Photography.

MORRIS, PERCY A. Nature Photography Around the Year. 1938.

Physics.

DAVIS, A. H. Noise. 1937.
EINSTEIN, ALBERT, AND LEOPOLD INFELD. The Evolution of Physics. 1938.
LEFEVRE, R. J. W. Dipole Moments. 1938.
OSGOOD, WILLIAM FOGG. Mechanics. 1937.
SEELIGER, RUDOLF. Angewandte Atomphysik. 1938.
SEWIG, RUDOLF. Handbuch der Lichttechnik. Teil 1–2. 1938.

Railroad Engineering.

Association of Railway Electrical Engineers. Proceedings. Volume 10. 1918.

Refrigeration.

WOSTREL, JOHN F., AND JOHN G. PRAETZ. Household Electric Refrigeration. First Edition. 1938.

Sanitary Engineering.

WILLIAMS, GEORGE BRANSBY. Storage Reservoirs. 1937.

Scientific Essays.

DAVIS, WATSON. The Advance of Science. 1934.

BOOK REVIEWS.

THEORIE UND ANWENDUNG DER LAPLACE-TRANSFORMATION, von Gustav Doetsch. 436 pages, illustrations, 15 × 25 cms. Berlin, Julius Springer, 1937. Price 34.50 R.M.

This book is volume XLVII of Die Grundlehren der Mathematischen Wissenschaften, a set of books with the special purpose of presenting the subject from the standpoint of its field of utilization. The author states that the student progressing through the general subject will eventually arrive at the place where it becomes apparent that certain facts bring a desire to make acquaintance with the Laplace-Transformation which on further pursuit will reveal the theoretical fundamentals and show at the same time the particular applications. When this degree is attained it will become evident that there are three courses to follow. The first is related to the Laplace-Integral $-\int e^{-st} F(t)\, dt$ with the limits o and ∞, respectively $-\infty$ and ∞, the latter being equivalent to the Mellin-Transformation.

The second is with the use of the Fourier-Integral and the third with the Laplace-Integral $-\int e^{-st}\,d\phi(t)$. This book starts in exactly at this point and is devoted to the first course and only incidentally mentions the second. It is divided into five parts. The first covers an introduction to the essential theory, a matter of some 184 pages. Parts two to five are devoted to the application side of the subject with more advanced explanatory theory where needed. This includes separate attention to the asymptotic relationship of the functions, and the employment of the functional equations through integral and differential methods.

The premises on which the author bases his work are listed in a comprehensive way, a sort of bibliography of abstracts. German-speaking students of mathematics with the proper background should find here much of interest.

R. H. OPPERMANN.

BIOGRAPHY OF BENJAMIN SMITH LYMAN, By Gonpei Kuwada. 104 pages, plates. Supplement—The Honest Rikisha Man. 10 pages, 13 × 20 cms. Tokyo, Sanseido Co., Ltd., 1937.

This is a life sketch of an American geologist by a Japanese with a Preface by Umekichi Yoneyama, a mutal friend of both.

Benjamin Smith Lyman was born in Northampton Mass., December 11, 1835. He graduated at the early age of twenty from Phillips-Exter Academy and from Harvard University in 1855.

His attention and interest in geology appears to have been inspired by his uncle by marriage, J. Peter Lesley, the distinguished geologist who founded and conducted the Second Geological Survey of Pennsylvania. When Lyman definitely determined to make geology his life work he was enabled, through the financial assistance of his uncle Edward Lyman, to study at the Ecole des Mines in Paris from 1859 to 1861 and later at the Royal School of Mines, Freiberg, Saxony; the latter being at that time the most distinguished and famous mining school in the world and at which not a few of the older generation of American mining engineers received much, if not all, of their technical education.

Lyman appears to have been variously employed in geological field work until 1870 when he was engaged by the British-Indian government in the oil fields of the Punjab.

In 1873 he was invited by the Japanese Government to become its chief geologist and mining engineer. He lived in Japan until 1881, his work there being distinctly the *magnum opus* of his life's professional activities. His biographer states (p. 14) that "when his government employment expired in 1879 Lyman remained in Japan, paying his own expenses until the Spring of 1881 straightening out what he could not finish during his term of employment and making reports on his various investigations." An observation which does not speak well for the generosity of the Japanese Government. It might be mentioned in this connection that Prof. Henry S. Munroe, long professor (1895–1915) of mining at Columbia University, New York, was Lyman's assistant on the geological work in Yesso, Japan.

When Lyman revisited Japan in 1907 he was photographed with a group of his former Japanese assistants (page 16). This picture is of unusual interest for an examination of their faces shows them to be of the very highest class of intellectual Japanese, distinctly, I should say, of the Samurai—the flower of Japan.

Lyman was not a rich man and his love for and interest in Japan was frequently manifested; thus his biographer mentions on page 14 "on leaving Japan for home he discovered that the Department of Engineering had no fund to publish his survey map of the oil-fields of Japan. So he paid for the publication and contributed the map to the Department." On page 17 he states "Mr. Lyman's work in Japan was his most noteworthy achievement because of its extent over a period of about nine years, and because of the high esteem and affection which resulted therefrom." "At no time since he left Japan have his assistants failed to keep in close touch with him, and during the later years of his life when his activities were limited, displayed their affection and high regard by sending him many substantial gifts." This tribute I know to be deserved and correct, for Mr. Lyman was one of my best friends, in fact distantly related to me through my marriage with the Dwight family of New Haven. Lyman was part and parcel of the intellectual aristocracy of New England which has given and done so much for the cultural development of the United States. Regarding Lyman's later professional and cultural life his biographer has drawn mostly from his diary and letters which together with his books are in the Forbes Library at Northampton. As was to be expected Mr. Kuwada appears not to have been acquainted with Lyman's activities in later life, especially the years in Philadelphia. Moreover, as Lyman was a very reserved man he told little of his personal affairs even to those who knew him as well as I did in his old age.

I knew he was employed on the Second Geological Survey of Pennsylvania under the direction of his uncle, J. Peter Lesley, but for how long and in what particular capacity I do not know. The record in "Who's Who in America" makes no mention of this fact. He wrote a number of technical papers which were published in the *Transactions of the American Institute of Mining Engineers*, probably the most notable of which was the Biography of J. Peter Lesley in 1903.

My own acquaintance with Lyman began in the late nineties, and was rather intermittent due to my long absence from home on professional work. However, owing to the relationship I have mentioned, he was a rather frequent visitor to my home and much beloved by my wife and children. His last days were sad, as he removed from Philadelphia and for sometime we did not know his whereabouts or that he was in want. We had previously supposed that although not rich he was possessed with sufficient to care for his declining years. Lyman was distinctly reserved and one could not ask questions regarding himself. He lived his quiet, intellectual and cultured life much to himself. Charming in its simplicity, not to say austerity, in selfless detachment to the great age of eighty-five. A character I sometimes think more appreciated by the Japanese who know him than by his fellow countrymen; certainly this is attested in the little book I am attempting to review and to the encomiums contained therein to which I am venturing to add my own.

In conclusion, a word about his biographer Gonpei Kuwada. This Japanese gentleman appears to have come to the United States when a boy and graduated from the Northampton High School in the year 1890. His excellent command of English attests that fact.

Lyman's great collection of books, maps, manuscripts, etc., is now in the Forbes Library at Northampton as a gift from his cousin Mr. Frank Lyman of

Northampton. A brief description of this remarkable assemblage of literary documents is mentioned by the biographer.

The little Supplement above mentioned is a simple folk story about Count Kuroda Kiyotaka, chief of the Hokkaido Kaitakushi, the office that opened up the resources of Hokkaido—the man with whom Benjamin Smith Lyman signed his contract.

F. LYNWOOD GARRISON.

Memorandum

Benjamin Smith Lyman became life member of The Franklin Institute on December 12, 1890; he served on Board of Managers during the years 1901–1902; he was a member of the Committee on Library from 1897 to June 1904, and its Chairman in 1903 and 1904. He made five contributions to the JOURNAL.

The following works by Mr. Lyman are in the Institute's Library:

Geology in Its Relation to Topography, 1857.
Japan, Geological Survey, Reports of Progress, Including Hokaido and Yesso, 1874–1879.
A Geological and Topographical Map of New Boston and Morea Coal Lands in Schuylkill County, 1889.
Report on the Shippen and Wetherill Tract, Schuylkill County, Pennsylvania, 1893.
Importance of Topography in Geological Surveys, 1900.
Vegetarian Diet and Dishes, 1917.

ALFRED RIGLING,
Librarian.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 615, Column Strength of Tubes Elastically Restrained Against Rotation at the Ends, by William R. Osgood. 38 pages, illustrations, 23 × 29 cms. Washington, Government Printing Office, 1938. Price 15 cents.

A study was made of the effects of known end restraint on commercially available round and streamline tubing of chromium-molybdenum steel, duralumin, stainless steel, and heat-treated chromium-molybdenum steel; and a more accurate method than any previously available, but still a practical method, was developed for designing compression members in riveted or welded structures, particularly air-craft.

Two hundred specimens were tested as short, medium-length, and long columns with freely supported ends or elastically restrained ends. The test specimens were centered under load on knife edges held in carriers, and the free lengths were computed by a rational method not heretofore used. Tensile and compressive tests were made on each piece of original tubing from which column specimens were cut. The column data were reduced with the aid of these tests, and formulas were constructed to represent the column strengths in terms of specified tensile yield strengths of the four materials used.

It was found possible to extend work done by Bleich on the design of elastically restrained compression members in bridges and to present a method that should be suitable for designing such members in aircraft. The design is facilitated greatly by the use of tables and a nomographic chart, both included in this paper. A numerical example is also given.

Report No. 620, Pressure Distribution Over Airfoils with Fowler Flaps, by Carl J. Wenzinger and Walter B. Anderson. 19 pages, illustrations, 23 × 29 cms. Washington, Government Printing Office, 1938. Price 10 cents.

Pressure-distribution tests were made of a Clark Y airfoil with a $0.20c_w$ Clark Y Fowler flap and of an N.A.C.A. 23012 airfoil with $0.20c_w$, $0.30c_w$, and

$0.40c_w$ N.A.C.A. 23012 Fowler flaps. Some of the tests were made in the 7- by 10-foot wind tunnel and others in the 5-foot vertical wind tunnel. The pressures were measured on the upper and lower surfaces at one chord section both on the main airfoils and on the flaps for several angles of attack with the flaps located at the maximum-lift settings. A test installation was used in which the model was mounted in the wind tunnel between large end planes so that two-dimensional flow was approximated.

The data are given in the form of pressure-distribution diagrams and as plots of calculated coefficients for the airfoil-and-flap combinations and for the flaps alone. The pressure-distribution tests show that the effect of increasing the chord of the Fowler flap, for a given lift of combined airfoil and flap, is to increase the portion of the total load carried by the flap and to decrease the adverse pressure gradients of the main airfoil and thereby its tendency to stall. The maximum values of the normal-force coefficient of the Fowler flap were found to be much smaller than previously indicated and approximately the same as those of the external-airfoil flap and of the simple split flap. The flap-load data given in this report supersede those given in Report No. 534.

COLLEGE PHYSICS, by Henry A. Perkins. 820 pages, illustrations, plates, 15 × 25 cms. New York, Prentice-Hall, Inc., 1938. Price $3.75.

Many texts on physics have appeared in recent years. Some have been devoted to special divisions of the main subject; some on certain degrees of the main subject such as elementary, intermediate or advanced; and some on the subject in general but placing emphasis on parts which are deemed worthy of such emphasis. This book belongs in the latter class. It is an elementary text which is designed to lead up to the intermediate stage. The outstanding feature of the book is clarity in presentation and this can best be explained from the author's statement in the Preface, "The purpose of this book is to give the student a substantial grasp of physical principles rather than to describe phenomena. The more difficult portions are therefore treated more fully than is usual in elementary texts." The difference between a mere description of nature and an explanation of nature is early brought out and may be said to represent the background of the entire book.

The subject is divided into the usual parts, mechanics, heat, wave motion and sound, light, electricity and magnetism, and corpuscular physics. Algebra and trigonometry are used throughout, vectorial representation being introduced at the very beginning. Each part is started from the usual sense manifestations and it progresses gradually through the more technical explanations. Modern ideas are given as far as practicable. Some material whose importance is largely historical has been retained and carefully used in maintaining interest and in making clear fundamental concepts. The use of diagrams and curves in conjunction with the text is not in the least restricted.

The formidable size of the book, some 803 pages, is explained by the lack of small sized type, a fact that often misleads an examiner into believing that a book is short. Small type is only used here at the ends of chapters to indicate supplementary reading and in problems for exercise. The problems reveal careful thought in their formulation both as to practicability and coverage of the chapter

subject matter. Answers are given. A subject index completes this interesting and useful book.

R. H. OPPERMANN.

ESSENTIALS OF ENGINEERING MATHEMATICS, by J. P. Ballantine. 572 pages, illustrations, tables, 16 × 23 cms. New York, Prentice-Hall, Inc., 1938. Price $3.75.

A great many students of engineering as well as schools of engineering are finding that there is urgent need for not only additional but a clearer conception of mathematics as a basis for the study of engineering. Those who must cope with engineering problems without sufficient mathematical background are certainly in difficulty. Therefore, when a book of the nature of the present one comes to hand, it calls for most serious attention. The author states that the main objective of this book is to introduce the calculus in a rigorous, practical form. His plan of accomplishing this objective would appear unusual to graduate engineers who recall the cut and dried sequence of subjects in mathematics during their period of studentship. Instead of placing the study of calculus at the top, or the end of the prescribed series of studies, in this book, the entire subject of the mathematical scope covered is studied in unity. Selections are made from algebra, trigonometry and analytical geometry which are best suited for furtherance of the calculus and after this, it is applied to the remaining parts of these fields.

The work starts with treatments on coordinates, functions, and angles. Then approximation calculus is taken up after which come derivatives and differentials and then integration. Trigonometry is taken up in full, passing to the straight line and circle, fundamental properties of curves, logarithms, trigonometric calculus, differentiation, three dimensions, and maxima and minima. There is much to be said in favor of this arrangement, keeping in mind the objective of the work, which is becoming more and more a necessity among engineers. Undoubtedly the calculus has been a stumbling block for many and a carefully laid out course of study such as this should be of great value.

The author shows much skill in his clarity in presentation. After the use of brief but effective introductions in plain understandable language he leads directly up to his point, not hesitating in the least to work out in detail illustrative problems. He conforms strictly to engineering mathematics with emphases on mathematics, for there is little mention of engineering made. This could have been done, with a possible greater resulting gain of enthusiasm, in the problems at the end of each chapter. The outstanding feature of these however is that the exercises check themselves.

The book contains a comprehensive subject index, tables of logarithms, and natural trigonometric functions. It could be used to advantage as a reference work, providing the user is familiar with its plan of arrangement.

R. H. OPPERMANN.

PRINCIPLES OF ELECTRIC POWER TRANSMISSION, by L. F. Woodruff. Second Edition, 257 pages, plates, illustrations, tables, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1938. Price $3.50.

The importance of electric power transmission is quite apparent to almost every citizen in this country today. The progress of the art has been very rapid,

for greater and greater distances are being covered with increasing dependability. To the electrical engineer in the technical aspects of the subject progress is much more evident. Practices of ten or twelve years ago are now much improved and design and operating procedures are greatly facilitated. Modern concepts of the subject make so much more possible while the saving of time and labor contribute to more accurate methods and reliability.

The book at hand is a second edition, the first having been published in 1925. According to the author, in this second edition, the text has been completely rewritten except for a few sections dealing with basic phenomena such as skin effect, in which no advances have taken place. A modern treatment is therefor to be expected. At the outset the general problem of power transmission is discussed; the size of the electrical industry, power transmission tendencies, requirements for satisfactory service, and essential features of transmission systems. After this the student is led directly into the problem itself; first by an explanation of the system of units known as the meter, kilogram, second (MKS) system for use in the derivations of inductance and capacitance; second by a discourse on inductance and reactance. Then there follow chapters on skin effect, the dielectric circuit, and steady-state currents and voltages on power transmission lines where there is included a preliminary treatment of the direct current case and a set of complex hyperbolic function charts. In the treatment of circle diagrams, the general circuit constants used in the text are used in the derivation of formulas and formulas are given whereby these may be expressed in terms of the constants of the equivalent π of the system.

Traveling waves, power limits and stability, mechanical principles, corona and insulators, and calculation of fault currents are all taken up in logical order. Diagrams, curves and tables are used profusely throughout the work. Supplementing the text there are lists of references and problems for exercise. The author does not hesitate to use illustrative examples and their process of solution in the text in order to clarify his points. There is a comprehensive index at the end of the book.

To electrical engineers who need an up-to-date text and reference work on electric power transmission, this book can be recommended.

R. H. OPPERMANN.

ELECTRON AND NUCLEAR PHYSICS, by J. Barton Hoag. Second Edition of Electron Physics. 502 pages, illustrations, tables, 15 × 22 cms. New York, D. Van Nostrand Company, Inc., 1938. Price $4.00.

Physical science in recent years has made tremendous strides particularly in the way of a fuller knowledge of the nature of the nucleus of the atom. This has been the result of untiring search and the results so far produced have been so successful and so promising that the work is going forward in a much more determined fashion in a great many places. But what of the student fresh from a course in physics or the physical worker who has not had the opportunity of becoming acquainted with new concepts, which both must face sooner or later? At this point a book of this nature becomes valuable. It is the purpose of the book to present experimental evidence of these concepts.

This book in addition to giving directions for performing the necessary experiments, dwells to quite an extent on the theory and meaning of the experi-

ments, a combination text and laboratory manual. It is divided into three parts, the first being devoted to electron physics. Here methods of measuring the electron charge, the mass and the wave-length are presented which is followed by photoelectric and thermionic emission. The collisions between charged particles is studied which yields a great deal of information as to the nature of the bodies themselves. Further revelations are observed when electricity passes through gases.

The second part of the book is on nuclear physics. Methods are presented showing that the isotopes of an element have atomic weights exceedingly close to whole numbers. Radiations and radioactivity, alpha, beta and gamma rays are treated as well as methods of accelerating ions and artificial transmutation. There is also a brief treatment of cosmic rays. Laboratory techniques is the heading of part three of the book. In this the production of vacua, pressure gages, the technique of small currents, and the detection of particles which includes photons as well as charged particles, are discussed.

In the back of the book a number of problems for exercise, tables of data, and a subject index is given. The method of approach used by the author is such that assists understanding, proceeding from the simple to the more complex so that reference is avoided at any point to discussions which appear later in the book. Both the old and new concepts of physical principles are recognized. The book should fit admirably well in its proposed niche to prepare for the study and practice of research in today's advanced knowledge of the field.

R. H. OPPERMANN.

ELECTRON OPTICS IN TELEVISION, with theory and application of television cathode-ray tubes, by I. G. Maloff and D. W. Epstein. First Edition, 299 pages, illustrations, tables, 16 × 23 cms. New York, McGraw-Hill Book Company, Inc., 1938. Price $3.50.

Radio undoubtedly ranks among the highest of modern scientific wonders. Yet, this is only one of the results we have today that is traceable to the discovery of the electron. It is often said that the world has only seen the beginning of what is sure to come from scientific work and development along these lines. Of the popular conceptions of what is in the offing, television is perhaps the best known and we are informed from time to time that much progress is being made in the solution of related problems. One of the leaders in scientific research and endeavor is the R. C. A. Manufacturing Co. The authors of the book at hand here give an account resulting from first hand experience at the Research Laboratories of this company on the subject of electron optics and cathode-ray television.

Written for the scientifically trained reader the book generally covers the theory of the how and why of the heart of television apparatus. In the introduction fundamental principles are briefly gone over. It tells the scope of the subject of electron optics, the essentials of scanning from its earliest conception, and the operation of the modern television tube. Thereafter the book is divided into two parts.

The first part is devoted to optics exclusively. To gain an engineering understanding of the theory of cathode-ray tubes, it is stated, the conception of the electron of modern quantum or wave mechanics is not essential and therefore only the classical conception is covered. After this the subjects of electron

emission is taken up wherein the subject is quite well discussed as far as its importance warrants with respect to television cathode-ray tubes. A very interesting but brief section is that on an analogy between electron optics and light. Here it is shown that while electron optics has nothing to do with optics in the ordinary sense of the word there is an analogy existing between the track of an electron moving through electrostatic and magnetostatic fields and the track of a ray of light in passing through refracting media. Under the subject of electrostatic lenses the focusing action of an electrostatic field is described and later magnetostatic focusing in cathode ray tubes by means of axially symmetric fields is covered.

Part two is devoted entirely to the television cathode-ray tube. It begins with the electron gun, the arrangement for generation, control and focusing the electron beam. Immediately following this, luminescent screens and deflecting screens are treated. There is a chapter on the classifications, ratings and characteristics of tubes, and one on such accessories as the relaxation oscillator and blocking oscillator.

The book is a remarkable development of the theory and its application in the television cathode-ray tube. No attempt is made to go beyond this. The plan and progression through the book are logical resulting in a comprehensive treatment of this very promising subject.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

A Text-Book on Crystal Physics, by W. A. Wooster. 295 pages, illustrations, 14 × 22 cms. New York, The Macmillan Company, 1938. Price $4.00.

Engineering Electronics, by Donald G. Fink. First Edition, 358 pages, illustrations, 15 × 23 cms. New York, McGraw-Hill Book Company, Inc., 1938. Price $3.50.

Master Builders of Sixty Centuries, by John Anderson Miller. 315 pages, illustrations, 14 × 21 cms. New York, D. Appleton-Century Company, 1938. Price $3.00.

Kontinuierliche Spektren, von Dr. Wolfgang Finkelnburg. 369 pages, illustrations, 16 × 24 cms. Berlin, Julius Springer, 1938. Price 33 R.M.

Combustion, Flames and Explosions of Gases, by Bernard Lewis and Guenther Von Elbe. 415 pages, illustrations, 14 × 22 cms. New York, The Macmillan Company, 1938.

Today's Geometry, by David Reichgott and Lee R. Spiller. 379 pages, illustrations, 15 × 23 cms. New York, Prentice-Hall, Inc., 1938. Price $1.84.

Duodecimal Arithmetic, by George S. Terry. 300 pages, tables, diagrams, 25 × 30 cms. New York, Longmans, Green and Co., 1938. Price $7.50.

Symposium on Consistency—Critical Discussion on Present-Day Practices in Consistency Measurement. Presented at the Fortieth Annual Meeting of the American Society for Testing Materials. 71 pages, illustrations, 15 × 23 cms. Philadelphia, Society, 1938. Price 85 cents.

Canada, Department of Trade and Commerce, Dominion Bureau of Statistics, Transportation and Public Utilities Branch. Statistics of Steam Railways of

Canada, for the year ended December 31, 1936. 212 pages, 17 × 25 cms. Ottawa, Minister of Trade and Commerce, 1938. Price 50 cents.

U. S. Department of Commerce, National Bureau of Standards. Research Paper RP1075, Radiometric Measurements of Ultraviolet Solar Intensities in the Stratosphere, by R. Stair and W. W. Coblentz. 30 pages, illustrations, 15 × 23 cms. Washington, Superintendent of Documents, 1938. Price 10 cents.

Canada, Department of Trade and Commerce, Dominion Bureau of Statistics, Census of Industry, General Manufactures Branch. Report on the Prepared Breakfast Foods and Other Cereal Products Industry in Canada, 1936. 9 pages. Forestry Branch, Estimate of Forest Production, Operations in the Woods in Canada, 1936. 10 pages. 2 pamphlets, 22 × 28 cms. Ottawa, Minister of Trade and Commerce, 1938. Price 15 cents each.

Great Indian Chiefs, by Albert Britt. 280 pages, plates, 13 × 22 cms. New York, McGraw-Hill Book Company Inc., 1938. Price $2.50.

Bell Telephone System, Monographs: B-1051, Transmission Measuring Systems for Telephone Circuit Maintenance, by F. H. Best. 16 pages, illustrations. B-1052, Cable Carrier Telephone Terminals, by R. W. Chesnut, L. M. Ilgenfritz and A. Kenner. 19 pages, illustrations. B-1053, On the Theory of Space Charge Between Parallel Plane Electrodes, by C. E. Fay, A. L. Samuel and W. Shockley. 31 pages, illustrations. B-1054, A New Single Channel Carrier Telephone System, by H. J. Fisher, M. L. Almquist and R. H. Mills. 22 pages, illustrations. B-1055, A Carrier Telephone System for Toll Cables, by C. W. Green and E. I. Green. 26 pages, illustrations. B-1056, Crystal Channel Filters for the Cable Carrier System, by C. E. Lane. 12 pages, illustrations. B-1057, The Impedance Concept, by S. A. Schelkunoff. 32 pages, illustrations. B-1058, Crosstalk and Noise Features of Cable Carrier Telephone System, by M. A. Weaver, R. S. Tucker and P. S. Darnell. 25 pages, illustrations. B-1059, An Application of Number Theory to Gear Ratios, by G. R. Stibitz. 10 pages, illustrations. B-1060, A Theory of Noise for Electron Multipliers, by W. Shockley and J. R. Pierce. 12 pages. B-1062, Composition and Structure of Hevea Latex, by A. R. Kemp. 11 pages, illustrations. B-1063, Ultraviolet Microscopy of Hevea Rubber Latex, by Francis F. Lucas. 21 pages, illustrations. 12 pamphlets, 15 × 23 cms. New York, Bell Laboratories, 1938.

National Advisory Committee for Aeronautics, Technical Notes: No. 644, Flight and Wind-Tunnel Tests of an XBM-1 Dive Bomber, by Philip Donely and Henry A. Pearson. 32 pages, illustrations. No. 645, Some Aspects of the Stalling of Modern Low-Wing Monoplanes, by Hartley A. Soulé and Melvin N. Gough. 13 pages. No. 646, Wind-Tunnel Tests of a 2-Engine Airplane Model as a Preliminary Study of Flight Conditions Arising on the Failure of One Engine, by Edwin P. Hartman. 55 pages, illustrations. No. 647, Engine Performance and Knock Rating of Fuels for High-Output Aircraft Engines, by A. M. Rothrock and Arnold E. Biermann. 34 pages, illustrations. No. 648. The Increase in Frictional Resistance Caused by Various Types of Rivet Heads as Determined by Tests of Planing Surfaces, by Starr Truscott and J. B. Parkinson. 15 pages, illustrations. 5 pamphlets, 20 × 26 cms. Washington, Committee, 1938.

CURRENT TOPICS.

Faint Flicker.—(*General Electric Review*, Vol. 41, No. 4.) A candle standing in the open a mile away is certainly a very weak source of light. At such a distance it produces, if it is a standard candle, less than 1/25,000,000 ft.-c. of light. And yet that infinitesimal amount of light is sufficient to control an electric motor—and not simply to start the motor but even to make it reverse its direction of rotation. The device so sensitive was described by J. L. MICHAELSON of the General Electric Engineering Laboratory, who at the annual meeting of the Inter-society Color Council in New York City recently told about the recording spectro-photometer, an instrument for precise measurement and determination of colors. Of course such a candle is not actually used, but Mr. Michaelson pointed out that even less than 1/25,000,000 ft.-c. change in light intensity is sufficient to cause the motor of the spectro-photometer to reverse its direction of rotation, and thereby to record automatically the varying percentages of different wavelengths of light reflected or transmitted by the sample under investigation.

R. H. OPPERMANN.

Wetter Water.—(*Heating and Ventilating*, Vol. 35, No. 4.) B. G. WILKES of the Mellon Institute of Industrial Research and J. N. WICKERT of the Carbide and Chemicals Corp. have announced chemistry's latest miracle, to the American Chemical Society at Rochester. A new synthetic alcohol added to ordinary water makes it "wetter." Whatever the water touches it wets almost instantly. Yarns that would take many minutes to become wet through with ordinary water, became soaked in a few seconds with "wetter water." Outstanding and probably most useful from the point of view of health among the properties of the discovery, is its capacity for laying dust. In this connection Mr. Wilkes stated that an ordinary water spray fell through the air of a room hazy with dust without effect. Wetter water, however, made the air almost entirely clear and solved the health hazard. The wet water simply soaked instantly every dust particle it touched, where ordinary water drops had been glancing off. This should be a great aid to air conditioning, as the fine sprays of ordinary water used in spray chambers should be made much more efficient through the use of

this substance. Wetter water also enhances the deadliness of most insect sprays. Old wallpaper starts peeling when touched by wetter water. The substance is also a good remover of the poisons left on fruits from insect sprays.

R. H. OPPERMANN.

Oiliness in Its Relation to Viscosity in Lubricants.—A. W. BURWELL AND J. A. CAMELFORD. (*National Petroleum News*, Vol. XXX, No. 16.) This relationship has been a question among petroleum technologists for two generations. In an effort to differentiate between these properties and to explain the meaning and application of the two forces in lubrication, a carefully developed study was undertaken. When a lubricant is at work in any system, regardless of any factors which may determine its efficiency, the actual composition of the film is not identical with the composition of the oil mass. The characteristics of the lubricating film are determined by the relative attraction for the metals comprising the bearing of each component of the mixture comprising the lubricant. Differences in coefficients of kinetic friction have been noted in many oils possessing the same general physical characteristics but of different origin. Also variations in refinery practice cause wide differences of lubricants derived from the same source. These are usually observed over the entire range of pressures and temperatures used. In some cases these variations in frictional qualities of films are of great importance even in the region of full fluid film lubrication. Observations were made of several instances where high viscosity lubricants produced such high coefficients of kinetic friction in this range that the internal friction of the films produced a gradual shearing off of the bearing faces, resulting in bearing failure. When tests were made on these same oils with identical bearing surfaces but under greatly increased pressures and temperatures very low coefficients of friction were obtained. It is believed that valuable information, which could be translated into rational fundamental dimensional terms would be gained from detailed experimental investigation of pressure-temperature-viscosity relations together with a study of the forces of attraction between bodies possessing known lubricating ability and the metals which commonly comprise bearing materials.

R. H. O.

Primitive Tin Metallurgy in Laos.—R. E. BARTHELEMY, in *Mining and Metallurgy*, Vol. 19, No. 377, gives a very interesting account of probably the only remaining tribal tin mining and

smelting. It is practiced by the Laotian natives in an area between Siam and Laos one of the five states forming French Indo-China. Here lives a small group of natives protected from the outside world by unexplored limestone cliffs and from civilization by the absence of roads and weather conditions, who are still making their peaceful living from fishing and tin smelting. Tin mineralization is all eluvial. When a favorable place has been found, it is worked by men who dig irregular holes and take back to the village only the highly mineralized rocks of hematite. Almost every house in the village has a crushing unit composed of a mortar hollowed out of a section of heavy hard red native wood, in which the ore is stamped to final washing size. The stamp is also made of this wood. The ore, crushed to size, is taken to the river for panning which is done exclusively by women using large batea pans made of light wood. The concentrate, carefully separated by hand, is stored for smelting. A crucible is dug into dry ground with air oven and blower arranged. The oven is charged alternately with concentrates and charcoal. When smelting is finished the oven is dismantled and the remaining embers and molten tin are stirred to clear the tin from dirt and ashes. After being cooled by water the spongy tin ingot is removed from the crucible and is ready for the Chinese traders. The average grade of ore treated is about nine per cent. tin, washing giving a 57 per cent. tin concentrate with 51 per cent. recovery A 94 per cent. metal is obtained from smelting although recovery is only about 41 per cent. owing to losses. The overall recovery appears to be not more than 20 per cent. On a large sample of low grade ore however the metallurgical results obtained by the natives were surprisingly good, a 24 per cent. concentrate which is about the table concentrate at the mills. Their recovery was about 40 per cent. This was probably due to the larger size of the sample.

R. H. O.

Combustible Gas Indicator Used for Detection of Hot Spots in Coal Storage Piles.—G. F. CAMPAN. (*Combustion*, Vol. 9, No. 10.) It has been the practice of The Detroit Edison Co. for a number of years to make routine surveys of its coal storage piles for detecting hot spots before spontaneous combustion occurs. The labor and time involved and the failure of the use of the thermocouple always to locate hot spots led to an investigation of another method of detection using a portable combustible gas indicator instrument. This equipment consists of an indicator calibrated for methane, a ¼ in. brass sampling pipe and 10 ft. of rubber hose. The pipe is closed and pointed at the bottom end to facilitate shoving into the

stock pile, with perforations on the sides near the bottom through which the gas sample is drawn. Routine surveys are made similar to the thermocouple method except that gas samples are taken at only one depth along the top of the storage piles. The instrument is calibrated to read 100 per cent. when the mixture of gas and air corresponds to the lower limit of explosibility in air. For methane this is 5 per cent. gas and 95 per cent. air. No fire has been found unless a reading of 30 per cent. or more of the lower explosive limit was indicated. However if a reading of 10 per cent. or more is indicated the area is explored with a thermocouple in an effort to locate the exact position of the hot spot. This seems necessary since any gas distilled from a hot spot down in the pile seems to diffuse over considerable area. This fact makes it comparatively easy to locate an area containing a hot spot by using a combustible gas indicator, whereas it might be missed if only a thermocouple were employed.

R. H. O.

New Absorption System for Low Temperature.—A. A. BERESTNEFF. (*Refrigerating Engineering*, Vol. 35, No. 5.) The ammonia-water absorption system has up to the present time found application in industrial refrigerating plants. This, however is handicapped by the necessity of providing a special rectifier to remove water from the ammonia vapor leaving the generator. Solid adsorbents have been tried but the difficulty arose that there cannot be operation in a continuous cycle unless two or more units work in succession. These difficulties seem to be eliminated by the discovery of a new binary system using ammonia as a refigerant and as an absorbent lithium nitrate instead of water. The discovery was the result of some investigational work done by a German concern, Gesellschaft fuer Drucktransformatoren in Berlin, and was described in Zeitschrift fuer gesamte Kaelte Industrie. Lithium nitrate which is solid by itself, forms a liquid solution when mixed with ammonia at atmospheric pressure and room temperature. The properties of the mixture have suggested a possibility of using it in a one-stage absorption machine for suction temperature reaching as low as $-85°$ F. An absorption refrigeration machine using $LiNO_3$ was designed and installed at Schering-Kahlbaum A. G. for $-67°$ F. After a period of 2500 hours of operation no chemical changes of the mixture could be discovered. The economics of such a machine compare well with an absorption machine using ammonia-water and with a conventional compression system as to operating cost. Regarding the first cost, the absorption machine using $LiNO_3$ has

been found to be very near the compression system of equal capacity and performance, which is possible due to the elimination of a rather expensive part, namely, the rectifier.

R. H. O.

New War Gases for Old?—MAJ. GEN. C. E. BRIGHAM. (*Army Ordnance*, Vol. XVIII, No. 108.) The belief is widespread that the next war will be won with new, mysterious, superdeadly gases. Every world power has engaged the services of chemical technicians who closely follow the progress of scientific research for its possible applications to military usage. Rumors have been rife as to the results of investigations regarding war gas. General improvements have been made, particularly applying to chemical devices, to the technique of their employment, and also to means of anti-gas defense; from which it does not necessarily follow that numerous new war gases have been developed. Many reports of revolutionary chemical agents are obviously products of fertile imaginations, while occasionally one appears that is worthy of study. An understanding of the requirements of a successful war gas will enable any intelligent citizen to discount the many rumors prevalent. A new gas must be useful to aid fighting forces and show a decided superiority to present standard gases in some important respect. This brings into play many factors besides the toxicity or inherent deadliness of various chemical substances. The availability and usableness must be considered. It must manifest its effects when present in the air in very minute quantities. Another requisite is that it should be difficult to protect personnel from the effects of the agent. It must be cheap, stable in storage and transportation, non-detectable, capable of being manufactured in quantity, and suitable for field usage. These and other requirements point to the fact that the reported discoveries of new gases of great power should be regarded with mental reservations. While these stories may provide a momentary thrill for the reader, they usually concern chemicals that have not passed the laboratory stage of development and in many cases not even the visionary stage.

R. H. O.

INDEX TO VOLUME 225.

January to June, 1938.

Algebraic equations. Mechanical solution of (Hart & Travis), 63

Atomic entities, significance of, in modern atomic structure (Swann), 289

Ballooning. Up in a balloon, boys (Jennings & King), 549

Bancroft, Wilder D. & Richard C. Clapp: Grotthuss and Einstein, 23

Battery, electric. An extremely light high-potential (Ramsey), 401

Beese, N. C.; J. W. Marden & George Meister: Measurement of light from a tellurium vapor arc, 45

Blair, Julian M. & Fred G. Person: Concerning the Herschel effect, 73

Book Reviews:

American Geophysical Union, Transactions, Eighteenth Annual Meeting, 1937, 367

American Institute of Mining and Metallurgical Engineers, Transactions, Volume 124, 110

American Institute of Mining and Metallurgical Engineers, Transactions, Vol. 125, Iron and Steel Division, 247

Association of Consulting Chemists and Chemical Engineers, Inc. Directory, 1938, 368

Ballantine, J. P.: Essentials of engineering mathematics, 771

Barrows, Wm. E.: Light, 370

Chemical Engineering Catalog, 1937, 112

Clark, C. H. D.: Fine structure of matter, 606

Doetsch, G.: Theorie und anwendung der Laplaee-transformation, 766

Dushman, S.: Elements of quantum Mechanics, 488

Ellis, C.: Chemistry of petroleum derivatives, Vol. 2, 369

Fieser, L. F.: Chemistry of Natural products related to phenanthrene, 107

Fisher, C.: Exploring the heavens, 111

Glasstone, S.: Recent advances in general chemistry, 106

Glasstone, S.: Recent advances in physical chemistry, 106

Green, S. L.: Hydro- and aerodynamics, 490

Hoag, J. B.: Electron and nuclear physics, 772

Klemgard, E. N.: Lubricating greases, 245

Kuwada, G.: Biography of Benjamin Smith Lyman, 767

Leyson, B.: American Wings, 608

Maloff, I. G. & D. W. Epstein: Electron optics in television, 773

Merrill, P. W.: The nature of variable stars, 246

Miller, J. A.: Milestones in medicine, Laity Lectures, 604

Morris, P. A.: Nature photography around the year, 607

Moulton, R. S.: National fire codes for flammable liquids, 607

National Advisory Committee for Aeronautics, Report: No. 602, 108; No. 604, 108; No. 607, 109; No. 608, 109; No. 610, 109; No. 611, 110; No. 612, 490; No. 613, 490;

No. 614, 367; No. 615, 769; No. 616, 368; No. 617, 609; No. 618, 610; No. 619, 610; No. 620, 769
Oswald, J. C.: Printing in the Americas, 105
Perkins, H. A.: College physics, 770
Reich, E. & C. J. Siegler: Consumer goods, 366
Rhine, J. B.: New frontiers of the mind, 243
Ruhemann, M. & B.: Low temperature physics, 489
Seaver, G.: Edward Wilson of the Antarctic, 487
Smoley, C. K.: Segmental functions, 366
Spratt, H. P.: One hundred years of transatlantic steam navigation 1838–1938, 609
Stetson, H. T.: Sunspots and their effects, 113
Stuart, C. E. & J. G. Pratt: A handbook for testing extra-sensory perception, 244
Von Buzagh, A.: Colloid systems, 605
Woodruff, L. F.: Principles of electric power transmission, 771

Clapp, Richard C. & Wilder D. Bancroft: Grotthuss and Einstein, 23
Colwell, R. C.; A. W. Friend & D. A. McGraw: The velocity of sound in air, 579
Condon, E. U.: Mathematical models in modern physics, 255
Conductivity measurements. The computation of ionization constants and limiting conductance values from (Shedlovsky), 739
Current Topics: 22, 44, 62, 94, 116, 170, 196, 226, 249, 262, 276, 288, 342, 350, 362, 400, 410, 436, 482, 493, 512, 548, 578, 584, 600, 613, 660, 708, 738, 776

Davenport, C. C. & R. P. Kroon: Spiral springs with a small number of turns, 171
Earth's electric field, polar molecules in, as absorbers of wireless waves (Holmes), 309
Einstein and Grotthuss (Bancroft & Clapp), 23
Electrodynamics of ponderable bodies (Slater), 277
Electrolytes, solutions of, in non-aqueous solvents (Kraus), 687
Electrolytes. The conductance of aqueous solutions of (Mac Innes), 661
Electrolytic solutions. Some aspects of the present status of the thermodynamics of (Harned), 623
Equilibrium. On physico-chemical states of (Finck), 411

Finck, J. L.: On physico-chemical states of equilibrium, 411
Fischer, Leander J. & James J. Ryan: Photoelastic analysis of stress concentration for beams in pure bending with a central hole, 513
Franklin Institute.
Bartol Research Foundation:
Communication no. 96: An extremely light high-potential battery of long life (Ramsey), 401
Notes, 585
Biochemical Research Foundation Progress (McDonald), 121
Financial Statements, 753
Library Notes: 103, 241, 364, 484, 602, 763
Medal Day Meeting, 745
Monthly meeting: December 15, 1937, 101; January 19, 1938, 237; February 16, 1938, 363; March 16, 1938, 483; April 20, 1938, 601; May 20, 1938, 745
Science and the Arts Committee. Abstracts of Proceedings: November 10, 1937, 102; January 12, 1938, 240, 484; April 13, 1938, 602
Friend, A. W.; R. C. Colwell & D. A. McGraw: The velocity of sound in air, 579

Functions, discontinuous. Operational representation of (Pipes), 53

Gases, efflux of, through orifices—Kinetic theory (Korvin-Kroukovsky), 81
Grotthuss and Einstein (Bancroft & Clapp), 23

Hall, William M.: The formation of systems of units, 197
Harned, Herbert S.: Some aspects of the present status of the thermodynamics of electrolytic solutions, 623
Hart, Harry C. & Irven Travis: Mechanical solution of algebraic equations, 63
Herschel effect. Concerning the (Person & Blair), 73
Holmes, M. C.: Polar molecules in the earth's electric field as absorbers of wireless waves, 309
Hopper, J. D.: Explosive characteristics of certain metallic picrates, 219
Hunt, R. M. & Parry Moon: Reflection characteristics of road surfaces, 1

Ionic reactions. Kinetics of (La Mer), 709
Ions in Solution, 623
Ionization constants, the computation of, and limiting conductance values from conductivity measurements (Shedlovsky), 739
Ives, Frederic Eugene (Jennings), 455

Jarnak, Poul: Violin, 315
Jennings, W. N.: Frederic Eugene Ives: A little tribute to a great inventor, 455
Jennings, W. N. & Samuel A. King: Up in a balloon, boys, 549
Johnston, John: Steel, 373

Keller, E. G.: Resonance theory of series non-linear control circuits, 561
Kemble, Edwin C.: Operational reasoning, reality, and quantum mechanics, 263
Kinetic theory. Efflux of gases through orifices (Korvin-Kroukovsky), 81
Kinetics of ionic reactions (La Mer), 709
King, Samuel A. & W. N. Jennings: Up in a balloon, boys, 549
Korvin-Kroukovsky, B. V.: Efflux of gases through orifices—Kinetic theory, 81
Kraus, Charles A.: Solutions of electrolytes in non-aqueous solvents, 687
Kroon, R. P. & C. C. Davenport: Spiral springs with a small number of turns, 171

La Mer, Victor K.: Kinetics of ionic reactions, 709
Light, measurement of, from a tellurium arc (Marden, Beese & Meister), 45

McDonald, Ellice: Progress of the Biochemical Research Foundation of The Franklin Institute, 121
McGraw, D. A.; R. C. Colwell & A. W. Friend: The velocity of sound in air, 579
Machine tools in America (Roe), 499
Mac Innes, Ducan A.: The conductance of aqueous solutions of electrolytes, 661
Marden, J. W.; N. C. Beese & George Meister: Measurement of light from a tellurium vapor arc, 45
Mathematical models in modern physics (Condon), 255
Matrix-operational methods in mechanical vibrations (Pipes), 343
Matrix solution of polynomial equations (Pipes), 437
Meister, George; J. W. Marden & N. C. Beese: Measurement of light from a tellurium vapor arc, 45
Moon, Parry & R. M. Hunt: Reflection characteristics of road surfaces, 1

Mulder, Peter J.: Growth and decay of phosphorescence in calcium sulphide by a photoelectric method, 527

National Bureau of Standards: Notes, 95, 227, 351, 473, 587, 745

Operational reasoning, reality, and quantum mechanics (Kemble), 263

Person, Fred G. & Julian M. Blair: Concerning the Herschel effect, 73
Philosophical concepts in modern physics, 255
Phosphorescence, growth and decay of, in calcium sulphide by a photoelectric method (Mulder), 527
Photoelastic analysis of stress concentration for beams in pure bending with a central hole (Ryan & Fischer), 513
Physics. Modern, philosophical concepts in, 255
Picrates, metallic. Explosive characteristics of certain (Hopper), 219
Pipes, Louis A.: Matrix-operational methods in mechanical vibrations, 343
Pipes, Louis A.: Matrix solution of polynomial equations, 437
Pipes, Louis A.: Operational representation of discontinuous functions, 53
Polar molecules in the earth's electric field as absorbers of wireless waves (Holmes), 309
Ponderable bodies. Electrodynamics of (Slater), 277
Publications received: 114, 247, 370, 491, 610, 774

Quantum mechanics (Kemble), 263

Ramsey, W. E.: An extremely light high-potential battery of long life, 401
Reality (Kemble), 263
Reflection characteristics of road surfaces (Moon & Hunt), 1
Resonance theory of series non-linear control circuits (Keller), 561
Road surfaces. Reflection characteristics of (Moon & Hunt), 1
Roe, Joseph W.: Machine tools in America, 499
Ryan, James J. & Leander J. Fischer: Photoelastic analysis of stress concentration for beams in pure bending with a central hole, 513

Shedlovsky, Theodore: The computation of ionization constants and limiting conductance values from conductivity measurements, 739
Slater, J. C.: Electrodynamics of ponderable bodies, 277
Solutions, aqueous, of electrolytes. The conductance of (Mac Innes), 661
Solvents, non-aqueous. Solutions of electrolytes in (Kraus), 687
Sound, the velocity of, in air (Colwell, Friend & McGraw), 579
Springs, spiral, with a small number of turns (Kroon & Davenport), 171
Steel (Johnston), 373
Swann, W. F. G.: Significance of atomic entities in modern atomic structure, 289

Thermodynamics of electrolytic solutions. Some aspects of the present status of the (Harned), 623
Travis, Irven & Harry C. Hart: Mechanical solution of algebraic equations, 63

Units. The formation of systems of (Hall), 197
Up in a balloon, boys (Jennings & King), 549

Velocity of sound in air (Colwell, Friend & McGraw), 579
Vibrations, mechanical. Matrix-operational methods in (Pipes), 343
Violin (Jarnak), 315

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